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HYDROGEN AS A FUEL

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

An engineering Study of the technical problems expected with the large-scale introduction of hydrogen (H_2) as a fuel has been initiated. During the subject initial six-month period, information was gathered and evaluated regarding the generation and transportation of H_2 and its utilization as an engine fuel. Results and conclusions are tentative and subject to future revision. (cont'd-)

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Gas Generating Systems
Engines
Emission
Energy Conversion Efficiency
Energy Conversion Devices
Fuel Performance
Hydrogen Fuel
Multi-purpose Fuels
Piston Engines
Fuel Injection
Fuel Ingestion
Internal-Combustion Engines
Energy Conversion

20. cont'd.

H_2 generation by coal gasification, by electrolysis, and by thermochemical processes using nuclear heat sources was investigated. Despite the extensive coal reserves in this country, proven, commercially-viable coal gasification methods are not used. Some newer processes may have an impact in 5 years or so. Electrolytic generation theoretically takes place at high efficiency, and a number of competitive designs to reach this goal are evaluated. The thermochemical approach becomes more feasible as the nuclear-core-coolant temperature increases; fast-breeder reactors with their lower cooler temperatures won't be used, but high-temperature gas-cooled reactors have high potential.

Pipeline transmission of H_2 may be compromised by hydrogen embrittlement, but although "embrittlement" by H_2 might weaken the pipeline, shortcomings of existing pipeline compressors are the principal problems expected in this mode of H_2 transmission. In this light, a novel, "regenerative", compressor is discussed.

Reciprocating-engine performance parameters are related in this study to fuel properties, and this forms a rational basis for evaluating H_2 as a fuel. A comprehensive collection of published operating experience with reciprocating H_2 engines reveals they are capable of high-efficiency, low-pollution operation when fuel-lean mixtures are used, but suffer substantial power penalties unless supercharging or fuel injection can be used.

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ABSTRACT

An engineering study of the technical problems expected with the large-scale introduction of hydrogen (H_2) as a fuel has been initiated. During the subject six-month period information was gathered and evaluated regarding H_2 generation, transportation and utilization as an engine fuel, and are reported. Results and conclusions are tentative and subject to future revision.

H_2 generation by coal gasification, electrolysis and thermochemical processes using nuclear heat sources was investigated. In this country despite the extensive coal reserves, the proven, commercially-viable gasification is not used, although some newer processes might have an impact in 5 years or so. Electrolytic generation theoretically takes place at high efficiency, and a number of competitive designs to reach this goal are evaluated. The thermochemical approach becomes more feasible at the nuclear core coolant temperature increases, fast-breeder reactors probably can't be used but high-temperature gas-cooled reactors can.

Although "embrittlement" by H_2 might weaken the pipeline itself, the principal problem expected in this mode of transmission appears to lie with existing compressors. A novel, "regenerative", compressor is discussed in this regard.

Fundamental relationships between fuel properties and reciprocating engine performance parameters are established and form a rational basis for evaluating H_2 (vs. gasoline) as a fuel. An extensive review of published results revealed that H_2 was capable of highly efficient, low polluting operation of such engines when fuel-lean mixtures were used.

INTRODUCTION

This the First Semi-Annual Technical Report on Contract No. N00014-67-A-0202-0046 entitled, "Hydrogen as a Fuel". The intention of the program is to make an engineering study of hydrogen as a fuel, including its generation, storage, transportation, safety and utilization, especially the technical problems likely to arise with the introduction of hydrogen (H_2) on a large scale.

During this first 6 month period a variety of topics were studied. However, only those in which sufficient progress was made to warrant reporting are included herein. Any conclusions that are drawn as a result of this initial activity must be considered preliminary and subject to change.

The entire technical content of this report is organized into Appendices which are intended to be independent and complete in themselves. The technologies examined in each appendix are at different stages of development. Consequently, the approach to and treatment of these technologies varies from appendix to appendix.

Appendix A - Hydrogen Production deals with three means of H_2 production: "Hydrogen Production by Electrolysis";"Production of Hydrogen by Coal Gasification" and "Thermochemical Hydrogen Production". The first was prepared by D.P. Gregory and A.J. Konopka of the Institute of Gas Technology under a subcontract;it is an evaluation of the potential of various high-efficiency electrolytic techniques for H_2 production. The second was prepared by L. Kurylko; it deals with means of producing H_2 by coal gasification. The third was prepared by R.S. Magee; it is an evaluation of the potential of H_2 production by thermochemical processes employing nuclear heat sources.

Appendix B-Hydrogen Pipeline Transmission was prepared by J. W. Hollenberg. It deals with the technical problems to be considered if gaseous H_2 is transmitted by pipelines, especially the problems related to the compressors that are used to boost the pressure at various stations along the pipeline.

Appexdix C - Hydrogen-Fueled Engines was prepared by R.B.Cole and R.F. McAlevy,III. It deals primarily with reciprocating, spark-ignition engines and is an evaluation of H_2-fueled (and gasoline-fueled) operating experience on a fundamental basis, provided by relationships between engine performance and fuel properties.

TECHNICAL SUMMARY

The purpose of the subject program is to conduct an engineering study of the technical problems to be expected with the large-scale introduction of hydrogen (H_2) as a fuel and to recommend means for their solution. The areas of concern are H_2 production, storage, transportation, safety and utilization. The work reported herein was directed towards definition of the technical problems; it deals with current status of technology and/or ultimate potential depending on subject area. To date, storage and safety have received insufficient attention to be reported upon.

The general methodology involved was literature review, plant and laboratory visitation, technical meeting attendance, and telephone and written communication.

All of the technical content of this report is contained in the three appendices which are each complete and independent. That is, each could be considered a separate report covering certain aspects of (a) generation; (b) transportation and (c) utilization. Each appendix contains its own abstract and summary.

The results and conclusions that emerged from the subject six month initiation period must be considered preliminary and subject to future revision during further study.

Appendix A -- Hydrogen Production deals with H_2 generation by electrolysis, coal gasification and thermochemical processes.

Highly efficient electrolyzers are required if large-scale electrolysis of H_2 is to be economically feasible, owing to the ever-increasing cost of electricity. An analytical expression for electrolyzer efficiency is presented and the conditions required for maximum efficiency are discussed. A review of current technology reveals that much of the present effort in electrolyzer design is directed toward achieving the high levels of efficiency that are theoretically possible. Based on the information avail-

able, however, it was impossible at this time to discern one that is universally superior.

Coal gasification appears practical for near-term and intermediate-term H_2 generation in the U.S.A. because of this country's large coal reserves and the growing world-wide shortage of petroleum. Two proven processes are already in commercial use in other countries, the Lurgi process and the Koppers-Totzek process (the latter being preferred for high H_2 yields). However, neither process is currently used in this country. Instead, H_2 is generally produced by steam reforming of natural gas and petroleum liquids, apparently as a result of economic constraints. Coal gasification processes will have no significant impact on H_2 generation in this country for 5 years or so.

In the long term, H_2 generation by thermochemical water-splitting processes appears promising, using nuclear heat sources. For the chemical processes proposed to date sufficient fundamental information does not exist to permit selection of the most promising candidates. Generally, the thermochemical processes involve fewer reactions and higher efficiencies the higher the maximum temperature at which heat is available. Thus, the thermochemical H_2 generation will be feasible with high-temperature gas-cooled reactors (temperature of coolant between about 800^oC and 1000^oC) and probably is not feasible with the liquid metal fast-breeder reactor (coolant temperature between about 450^oC and 575^oC).

Appendix B - Hydrogen Pipeline Transmission, reviews this country's natural-gas transmission system in light of its potential use for gaseous H_2 transmission. Despite suggestions by others that pipelines could be weakened by H_2 "embrittlement", a 130 mile, 12" diameter pipeline has been in continuous H_2 service in Germany since 1938; H_2 is introduced at 600 psia and delivered at a minimum of 225 psia. It has no compressors, operating by "blowdown". Thus, there is no experience with H_2 pipeline compressors. The "regenerative" compressor is proposed for this

purpose, and its operation and historical development are discussed in some detail.

Appendix C - Hydrogen-Fueled Engines deals with fundamental relationships derived between fuel properties and engine-performance parameters; operating experiences with H_2-fueled, reciprocating, spark-ignition engines are also comprehensively summarized. Together, these provide a rational basis for evaluation of H_2 as a fuel. Numerous comparisons are made between H_2 and gasoline use; it is shown that H_2 operation allows high efficiency and low pollutant emissions along with a control possibility ("quality control") which is impractical with gasoline. However, to gain these advantages of H_2 operation, engines must be operated fuel-lean at, say, half the stoichiometrically correct fuel/air mixture ratio. Under such conditions, the chemical-energy content of the lean fuel/air mixture is reduced, substantially penalizing the work (or power) output of the engine. Conventional supercharging or cylinder fuel injection can compensate for such a power penalty while maintaining the advantages of H_2 use. From many viewpoints, H_2 is an attractive alternative to gasoline and other hydrocarbons as engine fuels. Hydrogen use deserves further investigation both experimentally and analytically.

APPENDIX A - HYDROGEN PRODUCTION

ABSTRACT

Hydrogen production by electrolysis, coal gasification, and thermochemical decomposition of water was investigated in an attempt to determine the current status of technology, ultimate potential and inherent technological problems associated with these approaches.

Much of the current effort in electrolyzer design is directed towards developing the high efficiency potential of electrolysis. There is no single type of electrolyzer that is universally held as superior. It appears that the various design philosophies could result in hydrogen generation techniques quite different in concept from each other, yet all of industrial significance in appropriate applications.

Coal remains the fossil fuel of the future. There are two major processes of coal gasification currently used commercially: the Lurgi process and the Köppers-Totzek process. None of these processes are currently used in the United States but are well proven in many installations worldwide. The Koppers-Totzek process is currently the preferred gasification process in applications when only hydrogen is required. New processes of coal gasification are not expected to make substantial changes in the presently used coal gasification techniques within the next five years.

It was concluded that hydrogen production by thermochemical processes employing nuclear heat sources has excellent potential to meet future hydrogen demands. However, since the majority of thermochemical cycles proposed to date are only in the early stages of development, extensive research and development will be required to advance currently proposed processes to commercial practice.

APPENDIX A - HYDROGEN PRODUCTION

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A.1 - BACKGROUND & INTRODUCTION

A.1.1 - General

Hydrogen has been discussed frequently in the recent past as a potential, highly flexible energy medium of the future. It is ecologically attractive and broadly usable and it can be produced from a virtually inexhaustible feedstock, i.e. water. Much has already been written about the long-range potential for the "hydrogen economy" (Ref. 1,2).

Perhaps the most important single factor influencing the large scale use of hydrogen resides in the production system. It must be competitive to alternate, clean energy media, both in terms of the costs and the impact on the use of resources and the environment.

Present means of commercially producing hydrogen in the U.S. are by steam reforming of methane and naptha, and partial oxidation of fuel oil. The majority of hydrogen currently produced in Europe is also made by steam reforming of petroleum fractions. Hydrogen can also be produced by electrolytic decomposition of water, but the present higher cost of this method restricts this approach to areas such as in Canada and Norway, where hydroelectric power is abundant.

Clearly, our decreasing natural gas and crude oil reserves indicate that we cannot afford to continue producing hydrogen by current practice, even to just meet the growing needs for use in ammonia production, oil refining, methanol production, etc. And for the potential of the "hydrogen economy" to be realized, hydrogen production will have to increase several fold over the current projections for the year 2000.

This section discusses three options for the production of hydrogen: electrolysis, coal gasification, and thermochemical decomposition of water. While electrolysis is the best developed of these technologies at present, the cost of producing hydrogen

by electrolysis is determined largely by the cost of electricity and as such has not been economically attractive. However, the possibilities of improved electrolyzer technology coupled with lower off-peak electric costs, make this method attractive for further investigation. Our vast coal reserves, insures that this resource will be a prime source for hydrogen and other synthetic fuels in the future. The various proposed processes for the production of hydrogen from coal are discussed. Finally, various schemes for the production of hydrogen from thermochemical decomposition of water are reviewed.

Other means for the production of hydrogen, e.g., biological production schemes, are not considered. It was felt that within the scope of the present program, these proposed schemes were not sufficiently developed to allow adequate analysis of their technical feasibility and inherent technological problems.

A.1.2 - References

1. Gregory, D.P., Ng, D.Y.C., and Long, G.M., "Electrochemistry of Cleaner Environments" J.O.'M. Bockris, Ed., Plenum Press, New York, pp. 226-279, 1972.

2. Marchetti, C., Chemical Economy and Engineering Review, Vol. 5, No. 1, pp. 7-25, 1973.

The following section entitled:

A.2 - Hydrogen Production by Electrolysis

was prepared for Stevens Institute of Technology by D.P. Gregory and A.J. Konopka of the Institute of Gas Technology, III Center, Chicago, Ill. 60616.

A.2 - HYDROGEN PRODUCTION BY ELECTROLYSIS

A.2.1 Introduction

Electrolytic production of hydrogen is the simplest and cleanest method for making hydrogen from water. An electrolytic cell operates with essentially no moving parts, can be designed to produce no by-products, and offers the physical separation of hydrogen and oxygen as well as the initial decomposition of water. In principle, cells can be operated at high pressure with no efficiency penalty, so that electrolysis also represents the most energy-conservative means of developing pressure in the hydrogen product. Several large electrolytic hydrogen plants, consuming upward of 100 MW, have been constructed and have operated successfully, while many thousands of smaller units are in use for special applications. However, electrolysis is not a major process for hydrogen production and is normally considered to be expensive and inefficient.

Why is there a reluctance to use electrolysis as a major hydrogen-producing process? Basically, because its primary energy source, electric power, is expensive and is only obtained at low efficiency from other energy sources. The electrolytic process itself is normally operated at efficiencies in the 60-75% range and at capital costs only a fraction (about one-fifth to one-third) of the cost of the power station needed to drive it.

Because electrolytic-hydrogen costs are dominated by electric-power costs, large electrolysis plants are located only where there is an abundance of cheap hydroelectric power. These plants have been optimized for low capital costs and normally operate at efficiencies lower than can readily be achieved in practice. As power costs increase, more effort must be expended to develop the high efficiency potential of electrolysis.

In the course of this study, we have drawn on published information, on trade literature, and on personal interviews with representatives of Electrolyser Corporation, Teledyne Isotopes, General Electric Company, Life Systems, Inc., and De Nora S.p.A., whose assistance we gratefully acknowledge. It is clear that the manufacturers of electrolyzer plants are in an industrially competitive business and are therefore not free to divulge proprietary information. It is also clear that various people and companies have considerably diverging opinions on the most favorable design concepts and technical approaches for electrolyzer construction, and that there is no single type of electrolyzer that is universally held as superior.

Because electrolyzers can be operated over a range of voltages and current densities, no hard figures can be quoted for efficiency of operation or for capital costs. Each system must be designed and operated according to its specific application, and no competitive manufacturer will willingly disclose such figures publicly. The economics of electrolytic hydrogen production are therefore extremely hard to come by and must be interpreted with care.

We wish to stress in this report that the electrolytic production of hydrogen is an already achieved commercial process that can no doubt be improved considerably, both in capital cost requirements and in energy efficiency, by appropriate research. Although electrolysis is not today's major source of hydrogen, the technology involved in many other large-scale electrochemical production processes is appropriate to much of the overall system design of an electrolysis plant. The entire world production of aluminum results from electrolytic plants, as does most of the current production of such heavy chemicals as chlorine, caustic soda, hydrogen peroxide, and several metals including copper, zinc, and nickel. Thus, electrochemical production is not a new and untried concept in industry, and the electrolysis of water is a process capable of the massive scale-up that would be needed if hydrogen became a significant fuel or energy carrier.

Three factors dominate the usefulness of an electrochemical cell for hydrogen production. One is the energy efficiency, related to the cell's operating voltage; another is the capital cost of the plant, related to the rate of hydrogen production from a cell of a given size. These two factors are closely interrelated. The third factor is the lifetime of the cell and its maintenance requirements, which involve the materials used in its construction and the operating conditions selected. In this report we will emphasize an analysis of these three factors, how they relate to each other and to current technology, and what needs to be done to improve them.

A.2.2 Theory of Electrolysis

If two electrodes are placed in water, hydrogen ions produced by self-ionization migrate toward the negative electrode — the cathode — and hydroxyl ions to the positive electrode — the anode.[1] Because water has a low ionization constant, it displays a relatively high electric resistance. Both the hydrogen and hydroxyl ions have very high mobilities, which provide low electric resistances. As a result, strong aqueous acid or alkali solutions are suitable ionic-transport media for electrolysis cells. Other electrolytes are not normally considered for use in cells because they, themselves, break down under electrolysis and yield undesirable by-products. Because of very severe corrosion problems encountered in the electrolysis of acids, present state-of-the-art industrial electrolyzers almost universally use low-concentration aqueous potassium hydroxide or sodium hydroxide.

The overall reaction for the decomposition of water is given by —

$$H_2O(\ell) \rightarrow H_2(g) + 1/2O_2(g)$$

This reaction can be broken down into the reactions at the anode and cathode.

At the anode, hydroxyl ions are discharged and form oxygen. The metal or metal oxide surface of the electrode enters into the reaction according to a proposed mechanism[1] that can be represented as follows:

$$OH^- + M^1O \rightarrow M^1O - O + H^+ + 2e^-$$

$$2M^1O - O \rightarrow 2M^1O + O_2$$

M^1 represents the metal surface of the anode, which is usually nickel or cobalt.

At the cathode, the water molecule is discharged on a metal surface according to the reaction —

$$2M^2 + 2H_2O + 2e^- \rightarrow 2M^2 - H + 2OH^-$$

$$2M^2 - H \rightarrow H_2 + 2M^2$$

M^2 represents the surface of the cathode, which is usually iron. The participation of the metal surface in anode and cathode reactions is important; changing the nature of the metal can profoundly affect the catalysis of the electrode reactions.

The overall process of water decomposition by electrolysis is the reverse of the combustion of hydrogen. Therefore, the theoretical amount of energy required per unit quantity of hydrogen produced is the same as the heat of combustion. Each hydrogen molecule is formed by the addition of two electrons to two hydrogen ions in solution, so that a direct relationship exists between the current passed (electron flow rate) and rate of hydrogen production (Faraday's law). Deviations from Faraday's law, which implies that 15.6 SCF* of hydrogen is produced per 1000 A-hr, is characterized by the electric current efficiency of the cell. The current efficiency in most cells approaches 100%. Any lower efficiencies experienced are the result of extraneous electrode reactions during the electrolysis, but theoretically, no alternative chemical reactions can occur except the recombination of hydrogen and oxygen in solution. A perfectly efficient cell would require 94 kWhr of electrical energy for each 1000 SCF of hydrogen produced. Of these 94 kWhr, only 79 need to be supplied as <u>electrical</u> energy; the remainder as heat. Since this energy input to the cell is in the form of power, the product of voltage and current, each electrolytic process has a theoretical voltage corresponding to the energy required for the reaction to proceed.

In electrolysis only the free energy of reaction, ΔG, can be interchanged with electrical energy at constant temperature and pressure. The quantity of electric charge corresponding to the molar quantities indicated in the balanced chemical equation is nF, where n is the number of electrons transferred per molecule and F is the Faraday value. If this quantity of electrical charge is transported through a potential difference of E volts, the amount of work required is given by nFE.[2] Since this electrical change does not involve pressure-volume work and is carried out isothermally, the change in Gibbs free energy is given by —

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* All cubic feet measurements given in this Appendix are at standard conditions, 68^0F and 14.7 psi.

$$\Delta G = -nFE \qquad (1)$$

where E is the potential difference or voltage, which by convention is taken as positive. Since ΔG is negative for a spontaneous cell reaction, and E for a spontaneously discharging cell is taken as positive, there results a negative sign in Equation 1. The electromotive force of a cell does not depend on the stoichiometric coefficient in the balanced chemical reaction, but the change in Gibbs free energy ΔG does depend on n, which in turn depends on how the chemical equation is written.[2]

The entropy change for an electrolytic cell reaction may be calculated from the temperature coefficient of the electromotive force since –

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = \Delta S$$

Introducing this into Equation 1, we have[2] –

$$nF\left(\frac{\partial F}{\partial T}\right)_p = \Delta S \qquad (2)$$

The enthalpy change for the cell reaction may be calculated by substituting Equations 1 and 2 into –

$$\Delta H = \Delta G + T\Delta S = -nFE + nFT\left(\frac{\partial E}{\partial T}\right)_p \qquad (3)$$

It is apparent from Equation 3 that the difference between free energy change and the total energy change (enthalpy) is accounted for by a change of entropy in the process. Since the entropy change cannot be converted to electricity, it must be supplied or liberated as heat.

We can calculate that for a water electrolysis cell the voltage corresponding to the enthalpy change, or heat of combustion of hydrogen, is 1.47 V at 25°C (77°F), whereas the cell voltage corresponding to the free energy change is only 1.23 V. This difference is important because it is a factor that works in favor of electrolyzers and against fuel cells.

In an ideal case, then, a voltage of 1.47 V applied to a water electrolysis cell at 25°C (77°F) would generate hydrogen and oxygen isothermally – that is, at 100% thermal efficiency with no waste heat produced. However, a voltage as low as 1.23 V would still generate hydrogen and oxygen, but the cell would absorb heat from its surroundings. The electrical energy required for the process is only 83.7% of the combustion

combustion energy of the hydrogen produced, the other 16.3% being supplied as heat. Another way of expressing this is that the fuel value of the hydrogen produced is 120% of the heating value of the electrical energy put in.[7]

In marked contrast to a hydrogen fuel cell, therefore, we see that under ideal conditions a water electrolyzer can have a theoretical "thermal" efficiency of up to 120%, while a perfect fuel cell is limited to an "electrical" efficiency no greater than 83.5%, if it operates at 25°C (77°F).[7]

The free energy change voltage, or "reversible" voltage as it is called, varies with temperature, as shown in Figure A.2-1. We can see that raising the temperature lowers the voltage at which water can be decomposed. Again, this factor operates in favor of electrolysis cells because at higher temperatures the electrode processes proceed faster, with lower losses, while the required energy input is less. This is in contrast to fuel cells; their available energy output falls as the temperature is raised.[7]

The voltage corresponding to enthalpy change, or, as we shall term it, the "thermoneutral voltage" varies only slightly with temperature, from 1.47 V at 25°C (77°F) to 1.50 V at 340°C (644°F). This is also shown in the figure. We can therefore identify three areas in which 1) no hydrogen is evolved, 2) hydrogen is made at an apparently greater-than-100% efficiency, and 3) hydrogen is made at less than 100% efficiency with production of waste heat.

A.2.2.1 Effect of Pressure on Decomposition Voltage

Considering the theoretical aspects of the effect of pressure on electrolysis, we have to inquire into the effect of pressure upon the decomposition voltage, the conductivity of the electrolyte, overvoltage of the electrodes, and concentration polarization. In the ideal case — obviously, a cell made up of a hydrogen and oxygen gas electrode — the electromotive force will be equal to the reversible decomposition voltage. The variation in the potential of a gas electrode with pressure is given by Helmholtz' equation[17] —

$$E = Eo + \frac{RT}{nF} \ln \frac{P}{Po} \qquad (4)$$

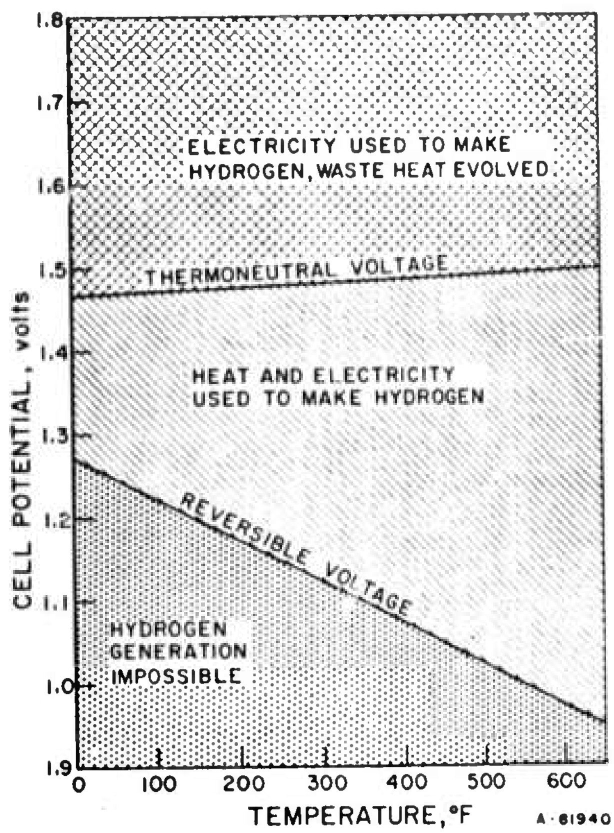

Figure A.2.1: IDEALIZED OPERATING CONDITIONS FOR ELECTROLYZER[4]

where Eo and E are the potentials at the pressures Po and P and $\frac{RT}{nF} \ln \frac{P}{Po}$ is the increment of potential due to a change of pressure (P − Po). By the usual convention, the Eo for a hydrogen electrode at atmospheric pressure is zero −

$$E = \frac{0.0577}{n} \log_{10} P$$

and at all pressures $\frac{E}{\log_{10} P}$ for a given gas electrode should be constant.

The effect of pressure on conductivity of the electrolyte can be expressed by the following equation −

$$\frac{1}{\lambda} \cdot \frac{\Delta\lambda}{\Delta P} = \frac{1}{V} \cdot \frac{\Delta V}{\Delta P} + \frac{1}{n} \cdot \frac{\Delta n}{\Delta P} + \frac{1}{a} \cdot \frac{\Delta a}{\Delta P} \cdots$$

Any change in the conductivity (λ) of an electrolyte implies a change in the number of ions and their mobility. This can only be brought about by altering the degree of dissociation of the electrolyte (a), its specific volume or compressibility, and/or its viscosity (n). The conductivity (λ) and the volume (V) of the electrolyte are both measured at atmospheric pressure.

A.2.3 Factors Affecting Electrolyzer Design

A.2.3.1 Operating Parameters

The theoretical decomposition voltage of water, calculated by thermodynamic laws, is 1.23 V at atmospheric pressure and 77^0F. A voltage above the theoretical value is necessary for the decomposition reaction to occur at a discernible rate. This excess voltage above the decomposition voltage is usually referred to as "overvoltage."

The overvoltage is made up of three principal components. One is the ohmic resistance of the electrolyte itself, another originates at the hydrogen-evolving electrode, and the third is associated with the oxygen-evolving electrode. Hydrogen overvoltage, then, is defined as the difference in potential between a hydrogen electrode at equilibrium and a hydrogen electrode subjected to cathodic current flow in the same electrolyte. Similarly, oxygen overvoltage is defined as the difference in potential between an oxygen electrode at equilibrium and one being anodized with an external current. Thus, the expression "overpotential" is sometimes used, instead of overvoltage or polarization, for individual electrodes. The amount of total cell overvoltage above the theoretical value of 1.23 V is dependent on the electrode construction and materials, the electrolyte resistance, and the amount and kind of foreign ions in solution. The energy efficiency of an electrolyzer can be measured by comparing its operating voltage with the theoretical value. The higher the applied voltage, the higher will be the rate of reaction, which produces a higher current. For most industrial electrolyzers, operating voltages in the range of 1.7-2.2 V per cell are necessary to decompose water.

In a comparison of various electrolyzer concepts, it is difficult to include all the factors that influence operating cost and efficiency. The designer of an electrolyzer will custom-design his unit to fit the exact conditions prevailing at the user's premises, so that two seemingly identical units from the same manufacturer may be operated under quite different conditions.

Because the current efficiency of most electrolyzers is almost 100%, the overall energy efficiency of hydrogen production is largely a matter of the operating voltage. We shall refer to the "thermal efficiency" of electrolysis as the cell potential corresponding to thermoneutral operation [1.47 V at 25^0C (77^0F), 1 atm] divided by the actual operating voltage. This corresponds to the ratio of the high heating value of the hydrogen produced to the electrical energy input. It is possible to operate a given electrolysis cell over a wide range of voltages or efficiencies, with a corresponding variation in current. An electrolysis cell has a specific current-voltage characteristic; the cell operates somewhat as a nonlinear resistor. As greater voltages are applied to the cell, greater rates of hydrogen production are achieved by sacrificing energy efficiency.

The amount of current flowing per unit area, or the current density at which a cell operates, determines the rate of hydrogen produced per unit area of electrode and is therefore an important factor in determining the unit cost of equipment for a given rate of production. Both the efficiency and unit cost can be changed by simply altering the operating conditions of the cell. Thus, there are tradeoffs among a) the operating voltage (efficiency), b) the rate of hydrogen production (current), and c) capital cost, all of which depend on the individual current-voltage characteristic of each type of electrolyzer. Selection of the optimum operating conditions for a specific installation depends markedly on the cost of electric power at that location.

Although the efficiency of operation can be adjusted during the life of an electrolyzer cell simply by altering the current and voltage at which it operates, such modifications will have a large effect on the output rate. Thus, the designer prefers to anticipate future changes in electric power costs by designing equipment to which additions can be made, if necessary, to keep production rates constant while the efficiency is raised.

Changes in electrolyte pH or concentration will naturally shift the reversible hydrogen potential. Since overvoltage is defined here as the difference in potential between the reversible electrode and the working electrode in the same solution, at the same pressure, and at the same temperature, the overvoltage must be expressed with respect to a reversible electrode subjected to the same conditions as the working electrode. If this definition of overvoltage is used, one observes in many metals the following dependence on pH: The overvoltage first increases with increasing pH, and then decreases again in alkaline solution. The maximum overvoltage is observed at about pH 8. It is pointed out in the Encyclopedia of Electrochemistry[9] that this variation of overvoltage with pH is surprisingly small considering that the concentration of the reacting species changes by many orders of magnitude.

The effect of increasing temperature in an electrolysis cell is to reduce the cell's operating voltage for two distinct reasons. One is because the electrode processes are speeded up at higher temperatures, which results in a lowering of the overpotentials at both electrodes. This is a true gain in efficiency of operation. The other is due to the reduction in the theoretical reversible potential for the cell at higher temperatures. However, as shown in Figure 1, the total enthalpy change of the reaction, shown by the "thermoneutral" voltage line, actually increases with temperature, so that even if the electric voltage is reduced, a correspondingly greater amount of energy is required to be supplied as heat. Overall, there is a net advantage in operating efficiency to be obtained by increasing cell temperatures, but this is offset by increased corrosion rates of the electrodes and the separator materials.

A number of advantages can be gained from operating an electrolyzer at higher pressures, including a) a reduction in specific power consumption, b) delivery of gas at pressure thus reducing or eliminating the cost of gas compressors, and c) reduction in the size of electrolysis cells.[1] It was shown in the previous section that the reversible cell voltage increases with pressure. However, the decrease in volume of the gases and the higher operating pressures result in a reduction in electrode overpotential, and there is usually a small overall reduction in the cell voltage. This real gain in efficiency is offset by increases in the costs of pressure vessels or stronger components.

A.2.3.2 Electrodes

To increase the operating efficiency, operating voltages can be lowered for a given current by using electrodes that carry precious-metal catalysts or that incorporate sophisticated metallurgical structures, both of which are expensive. The purpose of these sophisticated structures is principally to increase the actual physical surface area of the electrode without increasing the overall size of the cell. A roughened surface or a porous electrode with a high internal surface will achieve this objective. The purpose of a catalyst is to speed up the electrode reaction at the surface itself. Some electrodes incorporate both approaches, applying a catalyst to a highly developed surface.

When such expensive electrodes are used, the cell must operate at higher current densities, so that the capital cost per unit of hydrogen production does not rise beyond the economic limits. As current densities are increased, higher voltages are needed, and the gain, to some extent, is canceled. Thus, it is not an easy matter to compare the relative merits of a system that operates, for example, at 1.8 V and 100 A/sq ft of electrode with another that operates at 2.0 V at 100 A/sq ft unless the component costs are known and unless the importance of energy efficiency over capital costs is clearly defined.

Overvoltage and current density are empirically related. The dependence was first described quantitatively by Tafel in 1905 by the equation[9] –

$$n = a + b \log i$$

where i is the current density (total current divided by the absolute surface area of the electrode structure), n is the overvoltage, and a and b are constants that are dependent on temperature, surface state, and materials. Tafel lines, characterized by the above equation, are available for different materials and can be used as a reference in electrolyzer design, but the development of a high area surface, so as to reduce i, frequently dominates the variation in a and b due to material choice.

The influence of electrode material on overvoltage and the catalytic ability of certain metals to recombine hydrogen atoms was discovered by Bonhaeffer in 1924.[9] Both electrolytic hydrogen evolution and the catalytic recombination of hydrogen atoms depend on their energy of adsorption. It has been demonstrated that the hydrogen overvoltage, in general, decreases with increasing heat of adsorption. The adsorption energy, in turn, can be related to the cohesion energy, or sublimation energy, of the metals, and these, in turn, to electron concentration, surface energy, interatomic distance, compressibility, melting point, and electronic work function.

Electrochemical interfaces contain species other than protons and discharged hydrogen atoms. In particular, certain metals show a very strong affinity for water or oxygen, in fact, so strong that these metals cannot be plated out from aqueous solution. The discharge of hydrogen on such metal surfaces as molybdenum, tantalum, tungsten, zinc, niobium, chromium, and manganese proceeds with relative difficulty because of the strong affinity of oxygen for the surface. Cathodic polarization may not remove the oxide films or adsorbed oxygen species completely. The discharge of hydrogen gas will then take place on partially oxidized surfaces. Because the effect of the high adsorption energy of hydrogen on these metals is obscured by the strong affinity for oxygen, hydrogen overvoltage thus depends on the relative adsorption energy of protons and foreign species.[9]

A.2.3.3 Diaphragms or Cell Separators

The purpose of a diaphragm is to prevent adjacent electrodes from coming into electronic contact and to prevent the passage of gas from one electrode compartment to another without offering an appreciable resistance to the passage of current within the electrolyte. Gases might pass through the diaphragm between the compartments either as small bubbles or as dissolved gas, which would lead to a decrease in current efficiency and possibly to explosions. Dissolved-gas crossover is serious only in pressure operations, where the solubilities of the gases in the electrolyte are considerable. To prevent the passage of gas bubbles, the diaphragm must consist of small pores whose capillary pressure is greater than the maximum differential pressure applied across the cell.

If the diaphragm is not wetted by the electrolyte, the gas will collect preferentially in the pores, leading to an increase in resistance and eventually to the passage of gas. To prevent the passage of dissolved gas, for example, in pressure operation, the diaphragm must offer considerable resistance to flow of the electrolyte but, of course, a low resistance to current. These requirements are not as incompatible as they might appear because the electrolyte resistance will vary approximately as the reciprocal of the voidage or porosity of the diaphragm. The resistance to flow will depend on the actual size of the pores, the flow rate decreasing as the pore size is reduced.

Asbestos is the most common material used for diaphragms.[1] Electrolyzers operating at atmospheric pressure use woven asbestos cloth as diaphragms. Sometimes fine nickel wire is used to support the structure. Pressure electrolyzers usually have a mat or felt of asbestos fibers which produces a fine pore structure, giving a higher resistance to the penetration of gases. This mat is usually supported by the electrodes or by some other means.

Work is being carried out at DuPont and other organizations to improve and design new diaphragm materials.[16] The cost of improved diaphragms will be higher than for those made of asbestos. However, important savings in power consumption and cell maintenance appear possible.

In the process of designing electrolysis cells, certain important design features must be considered, which are enumerated here for general information[15]:

1. Thermodynamic properties such as heats of formation, free energies of formation, specific heats, activities, standard electromotive potentials, and reduction of these to the desired environment of electrolysis and equilibrium constants

2. Solubilities, composition-temperature diagrams, vapor pressures, and specific gravities of mixtures of electrolyte, water, hydrogen, and oxygen

3. Electrical conductivities of electrolytes versus concentration and temperature; conductivities of all current-carrying cell materials and electrodes

4. Polarization data and overvoltage versus current density for various electrolyte concentrations, temperatures, pressures, and electrode materials. The latter may be affected by various surface treatments, orientation and age of the electrodes, and trace impurities in the electrolyte.

5. Effect of gas bubbles (increase in cell resistance) and other suspensions on the conductivity of the electrolyte. As the current density or hydrogen-generation rate is increased, more gas bubbles are produced. The influence of gas bubbles can be reduced by optimum spacing of the electrodes or by the use of perforated electrodes, so that the gases escape from between them, or by operating the cell under pressure so the actual volume of the gas generated is reduced.

6. Diaphragm (electrode separator) properties including permeability, porosity, and relative resistivity.

7. Diffusion coefficients for atoms near electrode surfaces, both porous and nonporous

8. Thermal conductivities, heat-transfer coefficients, fluid properties, and viscosities for electrolytes and cell materials. Recent sophisticated studies have been carried out on fluid flow and heat transfer in water electrolyzers by Thorpe and Funk.[30]

9. Corrosion rates of materials of construction. These are affected seriously by the potential at which the material is operated, and are thus sensitive to the current density of operation. The temperature of operation is also a serious factor in determining corrosion rates.

A.2.4 Types of Electrolyzers – Current Status of Technology

A.2.4.1 Tank Electrolyzer

The oldest form of industrial electrolysis of water uses the tank electrolyzer,[24] in which a series of electrodes, anodes and cathodes alternately, are suspended vertically and parallel to one another in a tank partially filled, most commonly, with a 20-30% solution of potassium hydroxide in pure water. Alternate electrodes, usually the cathodes, are surrounded by diaphragms that prevent the passage of gas from one electrode compartment to another. The diaphragm, usually made of asbestos, is impermeable to gas but permeable to the cell's electrolyte. The whole assembly is hung from a series of gas collectors. A single tank-type cell usually contains a number of electrodes, and all similar electrodes of the same polarity are connected in parallel electrically, as pictured in Figure A.2-2.[26] This arrangement allows an individual

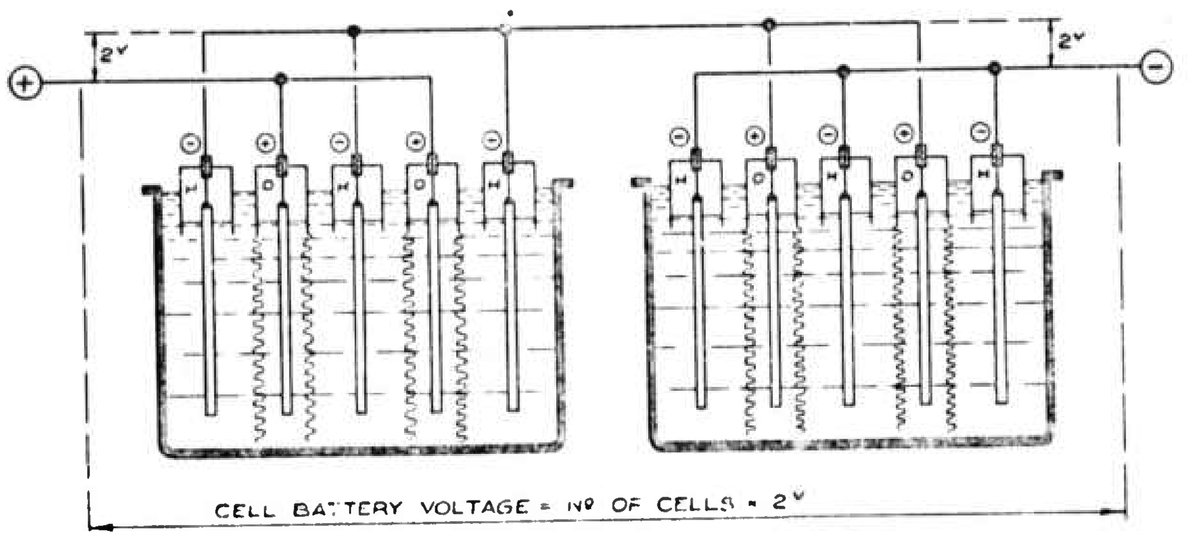

Figure A.2-2: SCHEMATIC DIAGRAM OF UNIPOLOR (TANK-TYPE) ELECTROLYZER

tank to operate across a 1.9-2.5 V dc supply.[24] In general, the costs of electrical conductors rise as the current load rises, but the cost of ac-dc rectification equipment per unit of output falls as the output voltage rises. This is one important consideration in the design of the tank-tyne electrolyzers. In general, a single silicon diode can handle voltages in the range of 500-1000 V and all the way up to its peak inverse voltage, which represents the maximum voltage to which the diode can be subjected.[1] Optimum rectifier operation is carried out at voltages just below the diode's peak inverse voltage, and since groups of tank-cell batteries can be connected in series, no electrical problem results.

The major advantages of tank-type electrolyzers are twofold:

1. Relatively few parts are required to build a tank-type electrolyzer, and what parts are needed are relatively inexpensive. Because of this feature, tank-type electrolyzers tend to optimize at a lower thermal efficiency than more sophisticated electrolyzer structures. Therefore, tank-type electrolyzers are usually selected when electric power costs are at their lowest.

2. Individual cells may be isolated for repair or replacement simply by short-circuiting the two adjacent cells with bus bar. This feature accommodates a minimum of downtime in producing hydrogen.

Some disadvantages of the tank electrolyzers are a) their size, requiring more floor space than other types of electrolyzers*; b) their inability to handle high current densities because they use cheaper component parts; and c) their inability to operate at high temperatures because of heat losses from the large surface areas of connected cells.

Performance studies have been carried out in India on tank-type electrolyzers where the electrolyte was open to the atmosphere to determine the effect of ambient temperatures on cell operating voltage.[22] These results prove that low cell operating temperatures also have a deleterious effect on cell operating characteristics. The lowering of cell temperatures, for example in winter, leads to a reduction in the conductivity of an electrolyte, resulting in a nonuniform current distribution. Greater resistance is then encountered in the current flow, resulting in an increase in cell voltage and reduction in gas output. A method of cutting off two cells from one end of the electrolyzer reduces the total resistance of the cell battery whenever the electrolyte temperature falls below a certain recommended operating point.

Tank-type electrolyzers that are open to the atmosphere also tend to absorb carbon dioxide at low electrolytic temperatures, causing the formation of solid carbonates that increase the electrolyte resistance and hence the cell voltage.[30] In performance studies, the electrolyzers experienced an electrolyte temperature fluctuation that followed the same pattern of fluctuation as the ambient temperature. The more common industrial tank-type designs of electrolyzers, however, have their electrolytes sealed from the atmosphere.

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* Some proponents of tank-type electrolyzers dispute this point, indicating that tank cells can be accommodated in as small a floor space as the filter-press type (described later). In actual commercial installations, however, tank-type cells appear to occupy large areas, though quantitative comparisons are not available.

A.2.4.2 Filter-Press Electrolyzer

As an alternative to tank electrolyzers that are "unipolar" or "monopolar," in which a single electrode is either an anode or a cathode, a bipolar electrolyzer exists in which one side of each electrode is used as an anode in one cell and the other side of each electrode functions as the cathode of the next cell.[8] Figure A.2-3 indicates the difference in the layout of electrodes in bipolar cell construction.

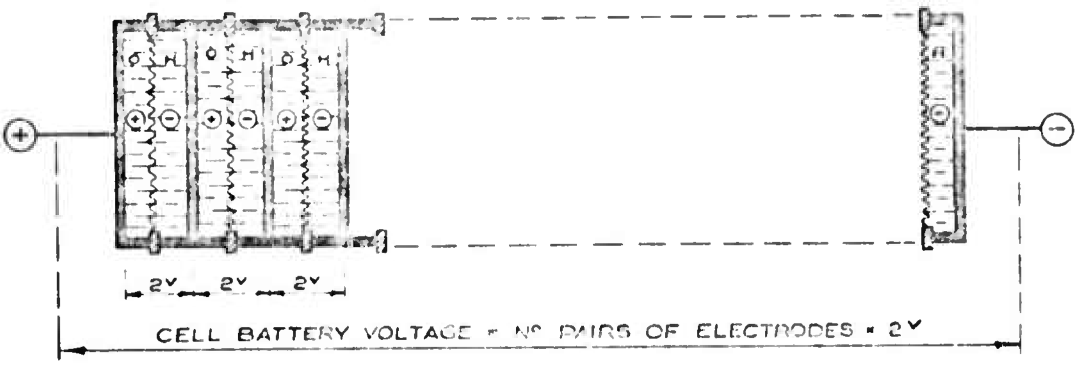

Figure A.2-3: FILTER-PRESS (BIPOLAR) CELL CONSTRUCTION

The bipolar arrangement is also known as the filter-press electrolyzer because of its superficial resemblance to a filter press, in which alternating layers of electrodes and diaphragms are clamped together. With a construction of this type, the cells are connected in series and individual cell voltages are additive within a battery. Because the cells of a bipolar electrolyzer can be made relatively thin, a large gas output is achieved from a relatively small piece of plant. It is usually desirable to circulate electrolyte through the cells, thereby separating the gas and the electrolyte, and in many designs this is accomplished in a separating drum mounted on top of the electrolyzer. The electrolyte, free of gas, is recirculated through the cells, the circulation being maintained by gas lift of the generated oxygen and hydrogen.

Although filter-press electrolyzers may be operated at higher current densities and appear to occupy relatively less space than tank-type electrolyzers, they require a much closer tolerance in construction and are more difficult to maintain. For example, in a filter-press electrolyzer, if an individual asbestos diaphragm is damaged, substantial rebuilding is necessary because the entire battery has to be dismantled and production potential is lost, whereas in a tank electrolyzer, a single inoperable cell may be isolated from a battery by means of a short-circuit bar and any necessary maintenance carried out while the full plant capacity is maintained, with only a slight increase in specific power consumption. Even though breakdowns in filter-press electrolyzers are rare, when they occur, rejuvenation is difficult and may take a considerable amount of time.[7] Filter-press electrolyzers usually also present greater capital costs than the tank-type electrolyzer. This is compensated for, however, since the filter-press type is able to operate at higher current densities (more hydrogen produced per area of electrode) with virtually the same operating voltages as the tank-type unit.

A.2.4.3 Stuart Cell

A typical example of the tank electrolyzer cell was developed, manufactured, and is being further developed by The Electrolyser Corporation, Ltd., in Toronto. A Stuart Cell,[4] as it is called, consists of a nickel-plated steel cell tank with positive and negative electrodes arranged alternatively and suspended from the cell cover. Electrodes in a single-cell tank are connected in parallel, and the cell tanks are connected in series to form a cell battery and to promote higher overall voltage and consequent lower rectification costs. This arrangement results in an operating voltage, even in large cells, of approximately 2 V dc. As is common with most tank-type electrolyzers, should repair of one cell become necessary, the modular construction of the cell battery permits the isolation of one tank from the line. A temporary bus-bar connection shorts out the damaged cell, and operation is continued until the damaged cell is repaired.

Electrodes used in these cells are made of high-conductivity, high-surface area, sand-blasted steel; the anodes are nickel-plated to prevent corrosion. As in most tank electrolyzers, each anode is surrounded by a woven asbestos cloth diaphragm which prevents the mixing of hydrogen and oxygen. It also guides the oxygen generated toward a storage chamber beneath the cell cover. Hydrogen formed at the cathodes rises between the diaphragms to the hydrogen compartment under the cover. It is not uncommon for these diaphragms to last well over 20 years before replacement.[27]

According to A. Stuart,[27] the unique and proprietary construction of the Stuart-cell electrodes provides a large surface for electrolysis in a minimum of space. Because of the large active surface of the electrodes, Stuart says, the cells are able to operate at a high total current, but the surface exhibits a low current density. Details of electrode construction are not available publicly.

The low cell operating voltage and the physical separation of each cell tank simplifies electrical insulation within each cell and enables efficient sealing against loss of electrolyte and gas product. The electrolyte is circulated independently within the cell by means of the lifting effect of the rising gas bubbles. This method requires no moving parts and avoids the hazards and complexity associated with external electrolyte pumping systems. A 10-15 yr or more life expectancy is appropriate before the electrolyte need be replaced. A 28% potassium hydroxide solution is the recommended electrolyte for the Stuart cell.

Each of the Stuart cells is supplied automatically with feedwater through individual valves set to maintain correct electrolyte levels and concentrations. A cooling-water header passes along the rear of the cell tank, supplying individual hydrogen and oxygen scrubbers at the cell-gas outlets and a cooling jacket on the back of each cell. The water flow is adjusted to maintain optimum cell temperature; the effluent water is suitable for recycling. As is common with many tank electrolyzers, the Stuart cell operates at a rather low temperature, 158°F (70°C) and low current density, which minimizes waste-heat production. With this arrangement, cell overall efficiency is higher at all levels of hydrogen output than it would be if operated at high current densities.

The Stuart cell is rugged and simple to assemble and maintain, and the component parts are fabricated cheaply. Hydrogen is produced at a purity of 99.9%. The oxygen by-product (99.7% pure), is produced in the ratio of one part oxygen to two parts hydrogen. Since the Stuart cell is contained in a closed system (not exposed to the atmosphere), no problem with the formation of potassium carbonate from carbon dioxide in the air is experienced.

The basic Stuart hydrogen plant is of modular construction in that an unlimited number of cells may be connected in series. By this method, hydrogen production capacity may be increased by simply adding more cells. Typical Stuart hydrogen plants produce hydrogen at the rate of tens of thousand cubic feet per hour. Some uses for this quantity of hydrogen output include the manufacture of semiconductor materials; hydrogen coolant at thermal and nuclear power stations; synthesis of chemical intermediates for long-chain polymer production; hydrogenation of oils and fats in margarine, shortening, and soap production; direct reduction of metal oxides; annealing of stainless and electrical steels; and float-glass manufacture.

The cells utilized in the hydrogen plants mentioned above are all of the described construction, but produce from 63.6 to 350 CF/hr per cell unit with a full loaded weight, ranging from 1665 to 5135 lb. The width of these cells is approximately 12-33 inches. The length of each cell is 44 inches, and the height is 49 inches. The hydrogen production in these cells for each 1000 A per cell is 15.9 CF/hr of hydrogen and 7.95 CF/hr of oxygen. The power consumption (dc) of each cell is 128 kWhr dc per 1000 CF oxygen. Maximum gas production pressure is slightly above atmospheric (10 inches water column).[4]

The operating costs of a Stuart cell may be inferred from the following cell requirements. For 1000 CF of hydrogen and 500 CF of oxygen, electric power consumption, including rectification, is 133-145 kWhr ac; demineralized feedwater required is 0.895 cu ft; and cell cooling water required is 38.77 cu ft. The cost of hydrogen and oxygen production is dependent on the cost of electricity and water supplies.

Smaller amounts of hydrogen may be obtained with the Stuart Packaged Hydrogen Generator. The generator is a self-contained, factory-assembled unit capable of producing pure hydrogen in quantities from 20 CF/hr to 1000 CF/hr with an ac power input of 3-140 kW, respectively. The dimensions of these units (in inches) are 25 X 48 X 58 and 48 X 232 X 74, respectively. Cooling water is not required for the 20 CF/hr plant and is 38.77 CF/hr for the 1000 CF/hr plant. An air-cooled silicon rectifier provides direct current to the cells.[3] Transformer, switchgear, and control equipment are also required. The transformer is needed to step down the alternating current to the necessary low voltage. Multiphase rectification is sometimes necessary to reduce the harmonic loading of the supply. Regulators control the voltage within 60-100% of the maximum needed output and give dependable variable control. The equipment is normally servo-controlled to give a preset output current and hydrogen production rate. If a hydrogen plant is to be expanded by the addition of more cells in series, a dual-voltage rectifier can be provided whereby either of two independent voltage ranges can be selected, so that the ratio of maximum to minimum volts will be the same on both voltage ranges.[24]

Some applications of these smaller units include hydrogen for laboratories, inflation of meteorological balloons, hydrogen and oxygen for cutting and welding, and the sintering of metal powders.

The Stuart units currently available typically absorb 24.6 kWhr/lb* of hydrogen produced, operate at 2.04 V, and have a thermal efficiency of 72%,[28] although current and voltage can be traded off to optimize production cost with electric power cost.

A.2.4.4 Teledyne Electra Cell

In 1967, Allis-Chalmers Corp. sold its fuel-cell and electrolyzer R&D technology to Teledyne Isotopes Co. Since then, Teledyne has entered the market with a number of electrolyzer cells.

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* A comparative table of electrolyzer operating characteristics is presented in Table A.2-1 (page 44).

The current Teledyne Electra Cell systems are of filter-press type and in general consist of modules made of multiple electrolysis cells connected electrically in series by common bipolar plates. The electrodes are separated by a matrix saturated with electrolyte. The matrix prevents mixing of the gases and provides a conductive path for the electrical current. As the hydrogen and oxygen are formed, they are kept apart, and the gases from each cell are ducted internally through manifolds to storage containers.[14]

This electrolyzer uses a potassium hydroxide-water solution (25% by weight) electrolyte with advanced-design porous nickel electrodes and operates at moderate temperatures, 100^{0}-200^{0}F. The cell contains no precious-metal catalysts.[11]

To support the electrolysis module, various subsystems recirculate and cool the electrolyte, add water, condition the product gases, and supply electricity.

Teledyne manufactures, or can build to order, three families of hydrogen-producing electrolyzers to suit a user's requirements: 1) generators that produce from 0.177 to 0.353 CF/min, 2) systems that produce from 0.177 to 7.06 CF/min, and 3) plants that produce tons/day.[12] Plants in categories 1 and 2 have been sold commercially, but plants in category 3 have yet to be ordered and built.

Small hydrogen generators produce from 0.177 to 0.353 CF of hydrogen/min. Uses for these amounts of hydrogen include carrier gases for gas chromatographs and fuel for flame ionization instruments, primarily in the pollution control and monitoring industry. These small generator units operate from a standard 110 V ac power source and deliver hydrogen at 0-35 psig with a purity of better than 99.99%.

A schematic diagram of the generator system is provided in Figure A.2-4. The electrolyte is recirculated on the oxygen side of the module to resupply each cell with water and to remove heat. The generation of oxygen gas in the cell provides a gas-lift effect for convective circulation, thereby eliminating the need for a pump. While auxiliaries are available to provide for continuous water replacement, the basic system operates on a batch feedwater refill technique. In most cases,

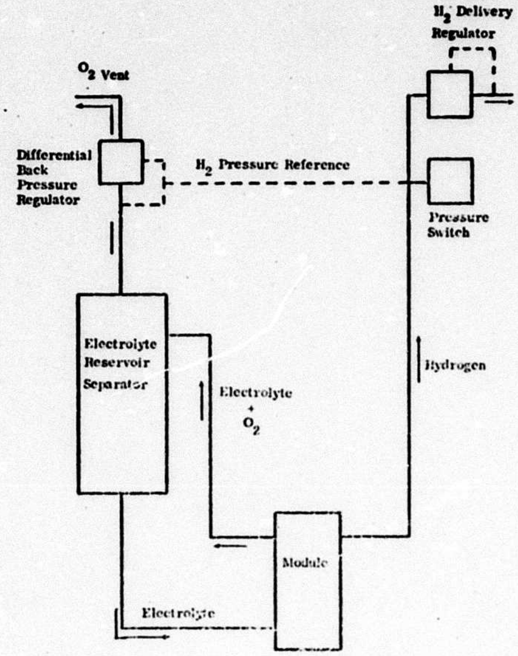


Figure A.2-4: SMALLEST TELEDYNE HYDROGEN GENERATOR[14]

heat is removed at the electrolyte reservoir by natural convection to the ambient air, allowing the system to operate at less than 130°F. The electrolyte reservoir also acts as a gas and liquid separator, allowing for the removal of oxygen and for pressure control of the oxygen and electrolyte portion of the system. Hydrogen generated at the liquid-free cathode is manifolded and ducted to a demand pressure regulator for subsequent delivery and use. A pressure switch senses the hydrogen pressure and controls a transformer and bridge rectifier to supply current when the hydrogen pressure is low. The system then maintains a preset pressure range with the module cycling off and on at a rate dependent on hydrogen usage.

This small system weighs about 50 lb and is 26 X 14 X 10 inches in size. The only facility interface required is standard a-c electric power. With this unit, high-purity hydrogen can be produced for as low as $3.10/1000 SCF based on an electricity cost of 10 mills/kWhr.[14]

Larger quantities of hydrogen are available with the Teledyne intermediate-size electrolysis systems. Where larger quantities of hydrogen are needed for industrial processing such as the production and sintering of metal powders of iron, nickel, cobalt, and molybdenum or for the bright annealing of stainless steels or electrical utility use, Teledyne intermediate-sized electrolysis units have been sized to provide from 0.177 to 7.06 CF of hydrogen/min. Increased capacity and optimum equipment utilization can be provided by the use of multiple units. Figure A.2-5 is a schematic diagram of the Teledyne intermediate-size hydrogen generator, which is capable of producing hydrogen with a purity in excess of 99.99%.

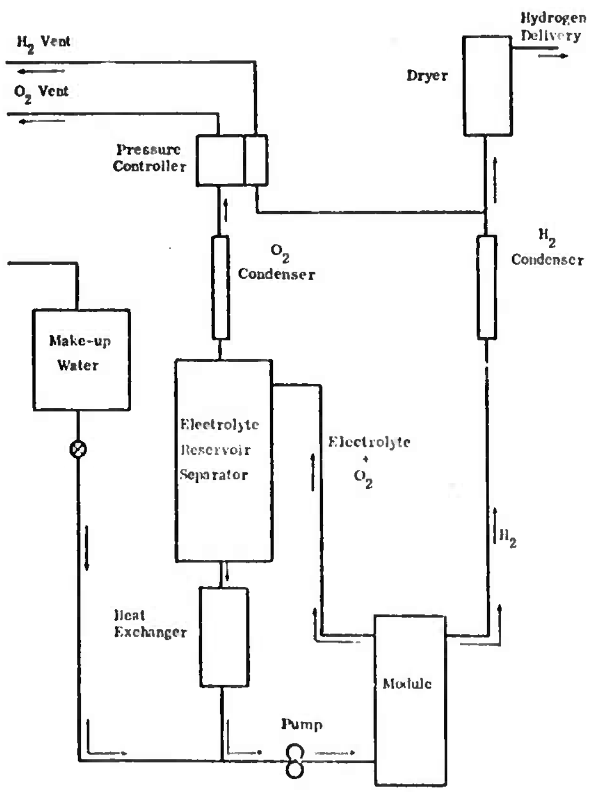


Figure A.2-5: INTERMEDIATE-SIZED TELEDYNE HYDROGEN GENERATOR[14]

With this system, which is similar to the smaller generator, electrolyte is recirculated on the oxygen side of the module by a centrifugal pump. This arrangement resupplies each cell with water, removes heat, and carries away generated oxygen. A tube-and-shell type heat exchanger is provided to transfer heat to a facility cooling-water loop. Normal system operating temperatures are less than 185°F. Oxygen is separated from the electrolyte in the reservoir, where water is also resupplied. The separated oxygen flows through a condenser to remove excess moisture and then flows to a pressure-control device to regulate and control the oxygen and electrolyte loop pressure. Hydrogen generated in the module is manifolded and piped directly to a condenser to remove most of the water vapor and then to a molecular sieve dryer to lower the dew point of the hydrogen to less than −110°F.[14]

Three-phase, 460-V ac power is converted and controlled by means of a silicon-controlled rectifier bridge. A pressure transducer senses the hydrogen pressure and signals a logic circuit, which applies current to the module at a level proportional to a preset pressure-range deviation. Thus, the unit continuously generates only the amount of hydrogen demanded. The system is normally set to deliver hydrogen at 70 psig, but can be adjusted to deliver gas at 100 psig.

A number of process monitors are incorporated into the system to provide fully automatic operations. Such parameters as temperature and concentration of electrolyte are controlled variables that aid safe operation and the necessary heat rejection. Start-up, shutdown, and safety parameters are continuously controlled. When power is applied to the system for start-up, an inert gas is provided to the system through a solenoid valve and forward-pressure regulator. This prepressurization gas pressure is monitored by a factory-preset pressure switch that prevents system start-up until 4 psig is maintained in the hydrogen system. During the initial period after start-up, several subsystems are sequentially activated and monitored to ensure proper general start-up. Following this period, power is applied to the electrolysis module and gas generation begins, allowing the prepressurization equipment to shut down. During any system shutdown, the hydrogen is automatically isolated from the gas-delivery manifold and the system will assume a standby condition and depressurize.[29]

These larger systems weigh from 1000 to 2000 lb per cabinet and have dimensions of 33 X 74 X 64 inches. Industrial 460-V ac three-phase electricity, cooling water, feedwater, and a small inert gas supply are the only other facilities additionally required. This system requires a minimum of maintenance attention. The electrolyte is sampled once per month to determine its specific gravity. After the initial electrolyte change at the end of the first month of operation, the electrolyte is only changed semiannually. Changing of the electrolyte filter, water-flushing of the solenoid valves, and calibration of the pressure switches are all recommended semiannually.[29]

Depending on the exact size and the application, these units will generate hydrogen continuously at an efficiency in the range of 28 kWhr/100 SCF to 17 kWhr/100 SCF.[14]

When quite large quantities of hydrogen are required in terms of tons per day, Teledyne recommends a considerably different system of hydrogen production. A schematic diagram of this system is shown in Figure A.2-6. In this system, electrolyte circulates to both sides of the electrolysis module, which allows more efficient heat removal and simplifies the pressure-control function. The electrolyte is recirculated by a single pump to both the hydrogen and oxygen cavities of the module. Each gas and electrolyte mixture is then returned to a different reservoir and separator, where the two phases are separated. The electrolyte is cooled in a heat exchanger and then mixed with electrolyte from the opposite portion of the system. Makeup water is continuously added at the mixing chamber. The gases are piped through condensers to remove excess moisture, then through a pressure-control device, and finally delivered for use. With this system of "double flooding" the gas-collection chambers, there is a) no pressure differential across the diaphragm or pushing away of the electrodes, which may occur with a large enough pressure differential; b) no concentration gradients across the cell, and therefore no concentration polarization; and c) a more economical production of hydrogen, since more hydrogen is being produced with the costs and requirements of auxiliary equipment remaining the same. Simple pressure-control devices are incorporated in this cell system to allow an operation of up to approximately 100 psig.[17]

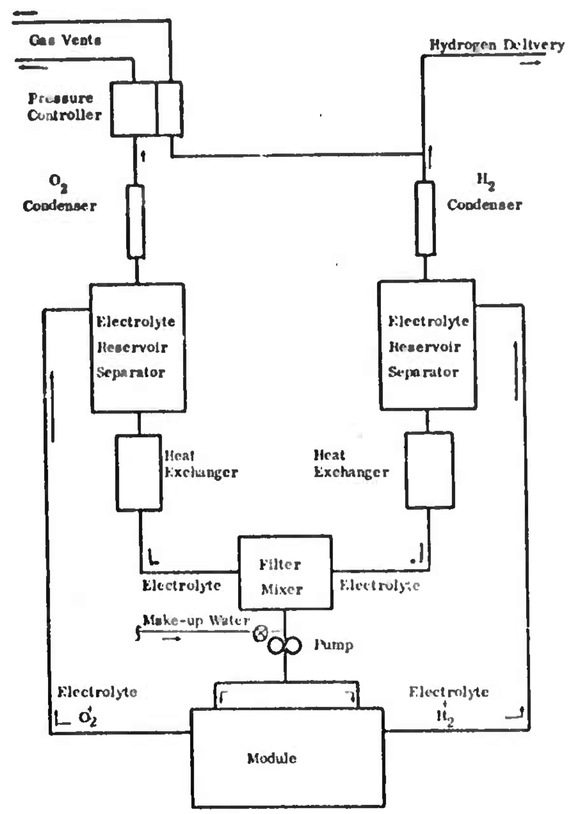


Figure A.2-6: LARGER-MODEL TELEDYNE HYDROGEN GENERATOR[14]

These systems can be controlled to provide constant gas-production rates and a specified level of gas purity. Multiple-system packages can be installed to supply virtually an unlimited quantity of hydrogen. Each system occupies approximately 260 cu ft of floor space and will generate hydrogen at an efficiency of 14 kWhr/100 SCF. With an electricity cost of 10 mills/kWhr, hydrogen can be generated at $1.40/1000 SCF.[14]

Although none have been built, Mr. W. C. Kincaide of Teledyne states that the hydrogen plants producing 1-4 tons hydrogen/day would operate at an electrical-conditioning efficiency of 95% and an electrolysis efficiency of 1.5 V/1.84 V, or 82%, 1.5 V being the "reaction enthalpy voltage." This specific plant, optimized for a power cost of 6 mills/kWhr-ton of hydrogen produced, consumes 1.95 MW (three-phase ac) of power, converts it to 5000 A at 370 V dc, and feeds it to a module of 201 cells, with the overall efficiency being 78%.[12]

Intermediate-sized units producing approximately 3.85 CF/min of hydrogen have an electrical conditioning efficiency of 92% and an electrolysis efficiency of 1.5 V/2.25 V, or 67%.

Teledyne's current electrolysis modules have overall thermal efficiencies between approximately 57 and 75%, with cell operating voltages of 2.4 and 2.1, respectively. The lower efficiency device represents the smallest electrolysis unit, used for gas chromatography, and the higher efficiency machine represents proposed large scale plants (in tons/day).[13]

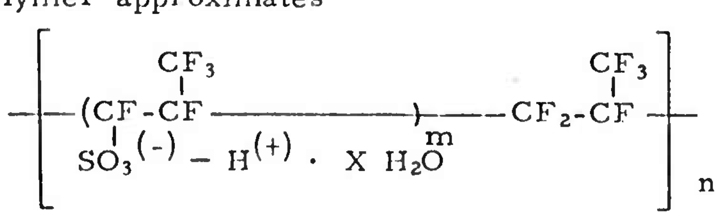
Teledyne is also developing high-pressure electrolysis units for military application, providing oxygen supplies for submarines. Its technique for developing 2000-3000 psi of pressure is to encase the entire cell battery in a stainless-steel pressure vessel which is flooded and pressurized with distilled water.

A.2.4.5 General Electric Solid Polymer Electrolyte Cell

General Electric Co. of Lynn, Mass., has been developing a water-electrolysis system based on solid polymer electrolyte (SPE) fuel cell technology. SPE fuel cells were first used in space during the Gemini Program, where they provided primary on-board power for seven of the spacecraft flights.

According to GE, certain technological advances in the design of solid polymer electrolytes (SPE) have resulted in a water-electrolysis unit of considerable simplicity in design and operation that can maintain stable and efficient use of relatively expensive electricity supplies.

The SPE is a thin, solid, plastic sheet of perfluorinated sulfonic acid polymer, having many of the physical characteristics of Teflon. Chemically, the polymer approximates[31] –



Unlike Teflon, however, when a thin sheet of this material is saturated with water, the polymer is an excellent ionic conductor, providing low electrical resistance. Used in an electrolysis cell, it is the only electrolyte required; there are no free acids or alkalies in the system. Ionic conductivity is provided by the mobility of the hydrated hydrogen ions ($H^+ X H_2O$), which move through the sheet of electrolyte by passing from one sulfonic acid group to another. Because the system is solid, the sulfonic acid groups are fixed, keeping the acid concentration constant within the electrolyte.

An important feature of the SPE system is the simplicity of the electrodes. Because the electrolyte is a solid, the catalytic electrodes are not required either to retain or support the electrolyte, and can therefore be optimized for catalytic activity at minimum cost. Currently, a thin layer of high-catalytic-activity platinum black is attached to the SPE surface to form the hydrogen electrode. A similar layer of proprietary precious-metal alloy catalyst forms the oxygen electrode. Additional metal current collectors are pressed against the catalytic layers. To date, the system has incorporated the use of niobium or titanium as the current collector and separator sheet materials. A schematic diagram of the SPE electrolysis cell is provided in Figure A.2-7.[21]

In this configuration, water is supplied to the oxygen evolution electrode (anode), where it is electrochemically decomposed to provide oxygen, hydrogen ions, and electrons. The hydrogen ions move to the hydrogen-evolving electrode (cathode) by migrating through the SPE. The electrons pass through the external circuit to reach the hydrogen electrode. At the hydrogen electrode, the hydrogen ions and electrons recombine electrochemically to produce hydrogen gas. An excess of water is usually supplied to the system and recirculated to remove any waste heat.

The gases produced by the SPE are generated in the stoichiometric ratio of hydrogen and oxygen at any pressure. The electrolyte sheet can withstand pressure differences of up to 1000 psi as well as high generating pressures up to 3000 psi by simply back-pressuring the system. These high generating pressures may be useful in solving transmission and storage problems.

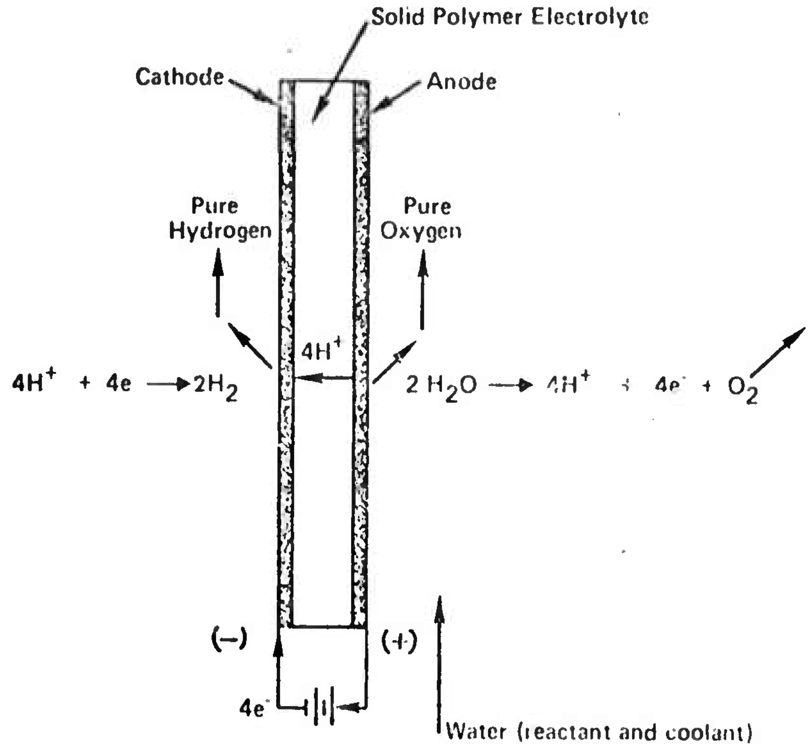


Figure A.2-7: SCHEMATIC DIAGRAM OF SPE ELECTROLYSIS CELL[21]

According to W. A. Titterington, manager of electrolysis development, the use of the SPE results in the following advantages:[20]

a. The cell can operate with high differential pressures (>1000 psia) in addition to high gas-generating pressures.

b. The concentration of the electrolyte is fixed, and the electrolyte is not mobile.

c. There is no possibility of acid carry-over into the effluent gas.

d. There are no corrosive electrolytes to control or leak in the system.

e. The electrolyte is essentially invariant in operation.

f. The acid SPE electrolysis unit results in a minimum power requirement per unit of gas generated.

g. High current-density capability can result in optimum design for low capital cost as well as low operating cost.

Although most of the SPE development was done in the past for the space program and aircraft applications, GE now produces two small hydrogen generators for commercial applications. Applications for these generators include the production of hydrogen for gas chromatographs, flame-ionization detectors, and other related areas. Operation of these units requires only 115/230 V ac 50/60 Hz power and a supply of distilled water. Both units have a hydrogen delivery pressure of 2-60 psig. One model sells for approximately $850, has two SPE cells with an area of 0.05 cu ft, and is rated at 0.005 CF/min hydrogen flow. The other model sells for $1000, has three cells of 0.05 cu ft area, and is rated at a 0.008 CF/min hydrogen flow. Both units require minimal maintenance, requiring only an occasional replacement of a desiccant cartridge and water deionizer.[6] The two units are both compact, weighing approximately 30 lb each and occupying less than 1 cu ft each. At present, 22 kWhr of power are absorbed per pound of hydrogen produced at an operating voltage of 2.00 and a thermal efficiency of 74%.[33]

A.2.4.6 Life Systems Cell

A static feedwater electrolysis system developed by Life Systems, Inc., under NASA sponsorship has been presented for potential applicability for terrestrial hydrogen production. Developed for the space program, the static water electrolysis system concept uses a) an alkaline electrolyte; b) a method whereby the electrolyte is retained in a thin porous matrix, eliminating bulk electrolyte; and c) a static water feed mechanism to prevent electrode and electrolyte contamination and eliminate the need of very pure feedwater.[10]

In the static water feed system, the water to be electrolyzed is fed to the cell electrolyte as a vapor. Each cell is divided into three main compartments: a water feed compartment, a hydrogen gas compartment, and an oxygen gas compartment. Compartment separation and liquid-vapor phase separation is achieved by the capillary action provided by liquid-filled asbestos sheets. Catalyzed porous nickel plaques support the cell matrix, forming a composite electrolysis site. Plastic screens similarly support the water feed matrix. The cell configuration is given in schematic form in Figures A.2-8 and A.2-9, which also show the cell operation. The bottom figure represents a thermally insulated box

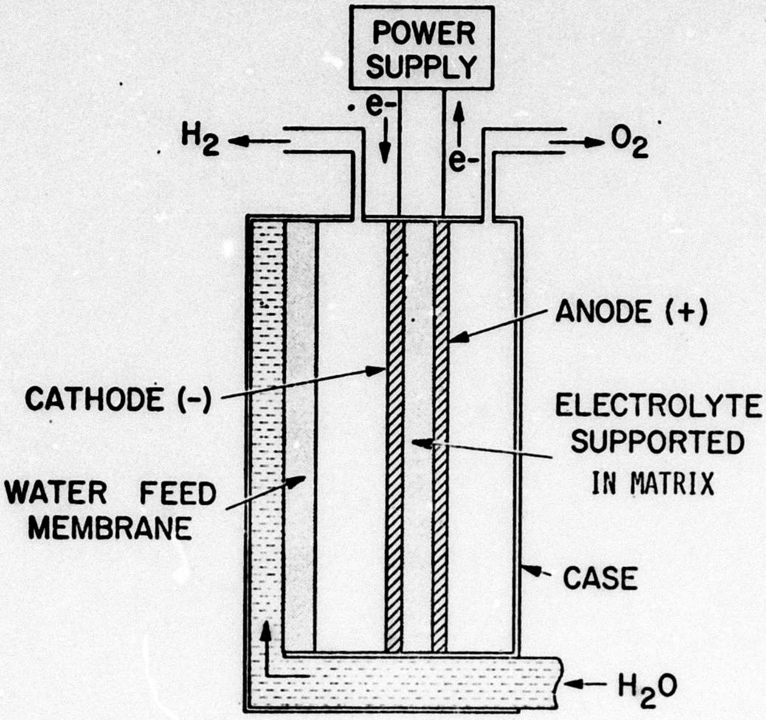


Figure A.2-8: LIFE SYSTEM'S CELL CONFIGURATION

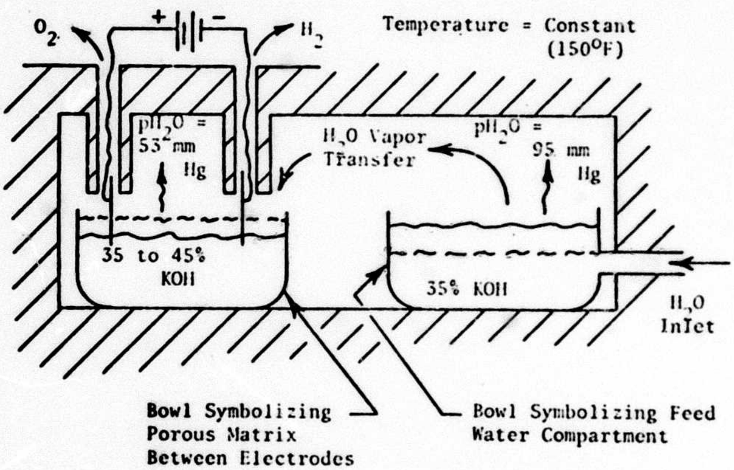


Figure A.2-9: LIFE SYSTEM'S CELL OPERATION

in which two bowls of electrolyte are sitting. When power is applied to the electrodes, water in the cell electrolyte is consumed. As a result, the concentration of the cell electrolyte increases, causing its vapor pressure to drop below that of the feed-compartment electrolyte. This differential in vapor pressure is the driving force that causes the water vapor to diffuse across the hydrogen cavity to the cell matrix.

Such a system is designed for zero-gravity operation. For terrestrial applications, the diagram in the lower figure would be one bowl of electrolyte and one bowl of feedwater.[10] Gravity applications require that the feedwater be drained out when the current is shut off, otherwise its higher water-vapor pressure would try to equalize the concentrations and flood the matrix. Two major advantages in this cell system became apparent: 1) the product gases need not be separated from the feedwater or electrolyte and 2) semipure water may be used, since contaminants rarely lower the vapor pressure of the feedwater. The electrodes and electrolyte remain uncontaminated since the water comes to the hydrogen electrode as pure vapor. The sole limit to impurities is the eventual blockage of the feedwater matrix pores. The amount of water transferred is directly proportional to the difference in water vapor pressures of the cell and feed electrolyte.

The cell design utilized in the static feed system includes a bipolar plate filter press construction with welded bus bars, providing intercell current connection. The hydrogen electrode is placed directly on the cathodic current collector. Current then flows from the cathode through the matrix to the oxygen electrode. An expanded nickel screen is placed on the back of the anode, providing both a path for the current and a space for oxygen evolution. The major portion of the inefficiency in the electrolysis of water occurs at the anode and must be removed as waste heat. The cell coolant passages were placed directly over the bipolar plate opposite the oxygen cavity. If air cooling is desired, this plate is extended out past the cell frame, forming external fins for convection or forced air cooling.[10]

Since Life Systems electrolysis designs were developed for the space program, expensive materials were utilized to provide reliability and efficiency. The system cell frames are injection-molded from high-flame-resistant plastic. All metallic parts are made from nickel alloy, which is then gold-plated. Both the feedwater matrix and the cell matrix are made of Life System's reconstituted asbestos. Other cell materials include stainless-steel end plate and polypropylene screens used to provide structural support for the matrices.[10]

The electrolyte used is a 35% potassium hydroxide-water solution instead of the more electrically conductive 25-28% solution.[10] At higher electrolyte concentrations and at higher temperatures, changes in concentrations between the water feed and the cell-matrix electrolyte give greater water-vapor partial-pressure differences. Since this difference is the driving force for the amount of water transferred, this phenomenon is accelerated.

Life Systems has developed two static feedwater electrolysis cell designs. One previous unit exemplified the simplicity of the static feed concept. The advanced system is undergoing parametric testing, including current density, voltage, and temperature relations; effect of pressure on cell voltage; and noble-metal catalyst loading amounts and techniques. Design capabilities of the present systems include —

Maximum pressure	600 psi
Maximum temperature	220^0F (with asbestos, long-term degradation starting at 200^0F)
Maximum current density	1000 A/SF — single-cell, short periods 600A/SF — multicell
Power requirement	117 kWhr/1000 SCF of hydrogen at 600 A/SF
Single-cell area	0.10 cu ft

A.2.4.7 Lurgi High-Pressure Cell[27]

Of the many electrolyzers produced in other countries, the Zdansky-Lants electrolyzers, manufactured by the Lurgi Company, are particularly noteworthy, since these electrolyzers, working under a pressure of 30 atmospheres, are very economical, compact, and reliable. The Lurgi electrolyzer is basically of the filter-press type.

In each cell of the electrolyzer, between two round, nickel-plated discs pressed in nickel-plated gaskets, are pressed reticular venting electrodes, diaphragms made of pressed asbestos, and sealing and insulating gaskets. The gas manifolds are located within the cells and are formed by rings of Teflon with holes for connecting the inner space of the cells to the gas channels. The cells are very narrow, making it possible to connect several hundred cells (up to 500 cells in the largest electrolyzer) into one relatively small apparatus.

Forced electrolyte circulation is used in the Lurgi electrolyzer. A pump forces cool electrolyte through an asbestos filter into the lower manifold of the cell bundle. The electrolyte is cooled in the gas separators by means of coils built into storage drums through which the coolant and condensate circulate. The condensate is pumped through a closed loop and is cooled in an adiabatic heat exchanger. The total volume of condensate in the cooling system of an electrolyzer consisting of 250 cells with a capacity of 10,543 CF/hr of hydrogen is 28.25 CF.

Hydrogen and oxygen are manifolded into separate collection chambers. A floating valve is installed in the oxygen gas separator to regulate the escape of oxygen and to maintain a constant electrolyte level in the gas separator. Desalinated feedwater is provided to the cells by means of the so-called variable-ratio pump, the capacity of which is adjusted manually, depending on the load of the electrolyzer.

If the electrolyte in any of the gas separator drums drops, the corresponding safety floating valve is opened and the gas whose pressure was too high is vented into the atmosphere. As the level in one of the gas separators continues to drop, a magnetic relay shuts the electrolyzer down.

During start-up of the Lurgi electrolyzer, the electrolyte, prepared in a tank in an atmosphere of nitrogen (to prevent absorption of carbon dioxide gas from the atmosphere) is heated in the makeup tank to 171°F and pumped into the electrolyzer. The gas separators are blown with nitrogen, during which the working and safety valves and relay are checked. The circulation pump is turned on and the flow rate of the electrolyzer is set by a rotameter (282.5 CF/hr for an electrolyzer with a capacity of 10,593 CF/hr).

The electrical load and pressure are increased simultaneously. When the current reaches a nominal level of 3000 A and the pressure increases to 30 atm, the gases are delivered. At this point, the feedwater pump and current stabilizer are turned on and the electrolyzer is brought up to normal operation. During normal operation, the electrolyte temperature in the apparatus is maintained at about 203°F and the pressure is 30-31 atm (regardless of the gas pressure used).

The low voltage on the electrolyzer cell of 1.8 provides a high efficiency of operation. Prolonged reliable operation of the apparatus with this low energy consumption is possible only if extremely pure water is fed to the cells.

After shutdown of the electrolyzer, the circulation pump continues to operate for 1 hour after the current is turned off. If the shutdown is for a period of more than 30 minutes, the electrolyzer is purged with nitrogen after the gas pressure is reduced. If the temperature of the electrolyzer drops to 104°F after shutdown, the electrolyte is heated or drained into the preparation tank. It is important that electrolyte draining does not take place earlier than 2 hours after depressurization, since considerable quantities of dissolved hydrogen and oxygen would otherwise be liberated from the solution into the alkali tank, producing flammable mixtures.

A.2.4.8 Cominco Cell

One of the largest hydrogen plants in the world is located in Trail, British Columbia, Canada. Although it has been shut down now for over a year because of rising power costs, this plant presents the first North American attempt at large-scale hydrogen production.

Individual cells are of Cominco patent design. The characteristic feature of this tank-type cell is a concrete top which supports the electrodes, the asbestos diaphragms, asbestos collecting skirt, feedwater pipes, bus bar, and gas-main connections. In this concrete cover also are the two gas chambers for hydrogen and oxygen and the narrow, inverted-trough-like collecting bins. The cell tank itself is made of iron, while the electrodes are made of mild steel plates and the anode is nickel-plated. The anode current density is 67 A/sq ft.[28]

This hydrogen plant contains 3229 individual cells, with a total theoretical hydrogen-producing capacity of 41 tons hydrogen/day. The cells operate at about 2.1 V, the current efficiency is close to 100% at atmospheric operating pressures, ac-dc rectification is provided, and the overall a-c power consumption is about 60,000 kWhr/ton of hydrogen.[19] Some cells have life spans of over 20 years, during which the usual operating temperature was 140°F.

According to J. N. Robinson of Cominco, "Our cell is very wasteful of floor space, and at today's building costs, it would probably be much cheaper to install a filter-press type of cell. On the other hand, we can cut out individual cells from overhaul without appreciable interruption of production, whereas if anything goes wrong with a filter-press unit it represents a substantial production loss and requires a long time to repair. Costs for operating labor and supplies should be quite low on any well-designed electrolytic plant, but costs for maintenance are likely to be high, the diaphragms being the weak point on all cells."[18]

Mr. J. Ross of Cominco mentioned that recent cell corrosion, leakage of hydrogen between anode and cathode spaces, and deterioration of concrete cell covers were problems associated with operation of the Cominco cell.[19]

A.2.4.9 De Nora Electrolyzer

The De Nora Co. of Milan, Italy, manufactures large industrial electrochemical processing plants and includes water-electrolysis in its range of products. Of the three large electrolysis installations built since 1945, De Nora built the 1,059,300 CF/hr plant at Nangal, India. (The other two are a 1,059,300 CF/hr plant in Norsk-Hydro, Norway, with its own Zdansky-type electrolyzers, and the 706,200 CF/hr plant at Kima, Egypt, built by Demag, of Germany.) All these units are of bipolar, filter-press construction.

The standard De Nora electrolyzer[3] consists of rectangular cells 16.4 feet wide by 5.25 feet high. These are stacked in series on either side of a cooling chamber and are surmounted by an electrolyte/gas separation unit. A photograph of a typical cell stack is shown in Figure A.2-10.

A unique feature of the De Nora design is the use of a double diaphragm. Two distinct layers of woven asbestos are used. These are in physical contact with each other, but the space between them is vented to atmosphere. In normal operation, the diaphragms are pressed against one another, but any penetration of gas bubbles results in the formation of a larger bubble between the diaphragms, which is vented to outside, and thus cannot intermix with the opposing gas.

Electrodes are single-layer sheet metal, perforated to allow gas exit, having a proprietary electrolytic surface treatment to develop a high surface area. No precious-metal catalysts are used. The electrodes are of low-carbon steel, and the anode is nickel-plated.

The Nangal plant consists of 60 units, each with 108 cells. Each cell stack is 16.4 x 5.25 x 49.2 feet in size and consumes 12,000 A at 2.2-2.3 V per cell, 250 V per unit, or 3 MW per unit. Thus, the entire plant consumes 180 MW dc.

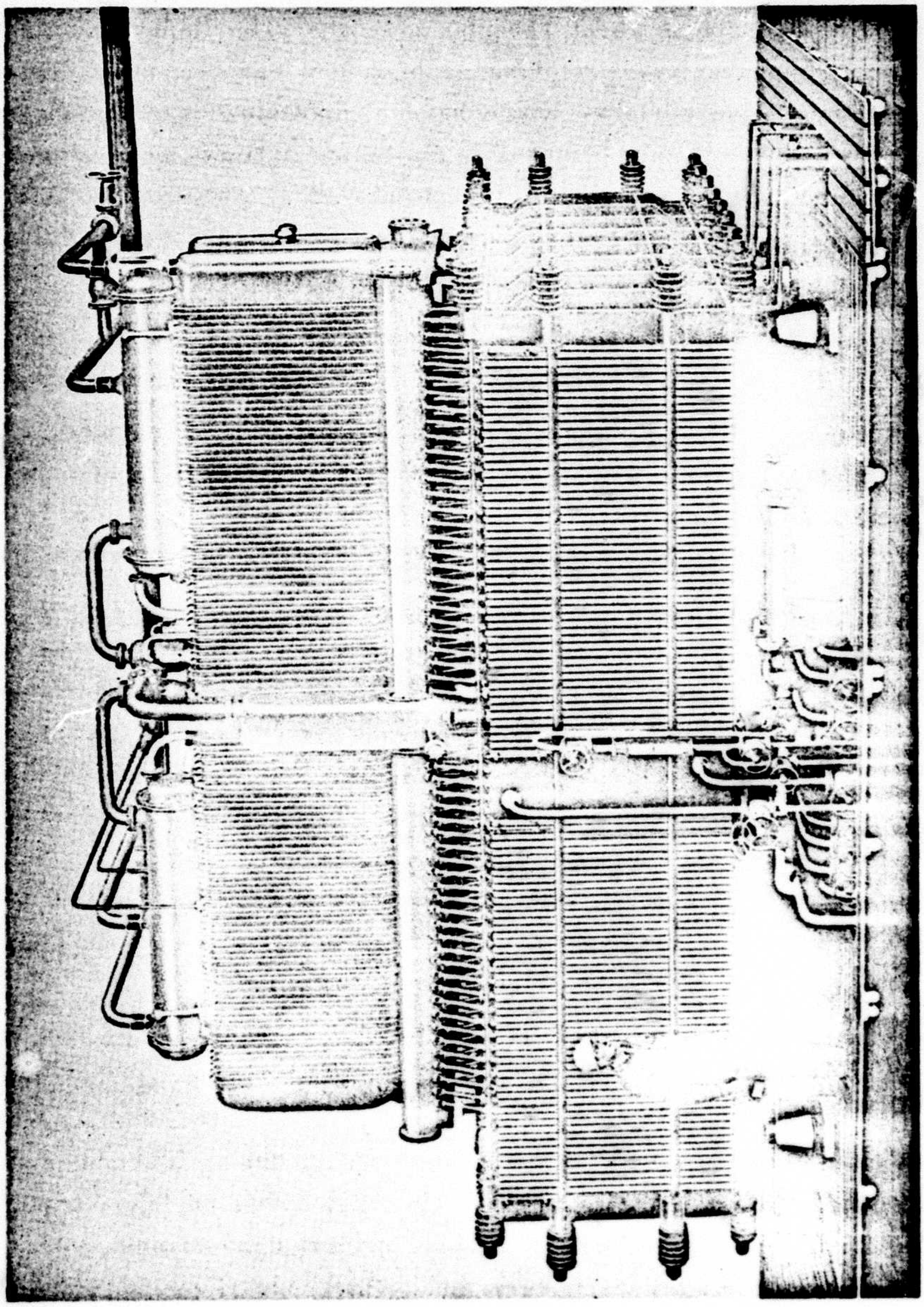


Figure A.2-10: DE NORA WATER ELECTROLYZER[3]

De Nora's standard cell sizes are of 2500 A, 4500 A, and 10,000 A capacity, and operate at about 180-200 A/sq ft. The Nangal plant, built in 1960, had a guaranteed performance of 2.1 V per cell at 10,000 A. Any new plant delivered today would have a guaranteed performance of 1.85 V at 12,000 A,[34] made possible by better activation treatment of the electrode. Future performance of 1.80 V at 18,000 A (300 A/sq ft) is believed to be possible by the incorporation of a homogeneous catalyst dissolved in the electrolyte, an approach which seems to be unique to De Nora.

A.2.5 Comparitive Evaluation of Various Electrolyzers

Figure A.2-11 is a comparison of cell operating performances of various advanced electrolyzers. These data are meant to give only a technological comparison of cell types and not of economics. A cell comparison based on voltage-current relationships is meaningless unless cell cost is included.

Interestingly, data are shown near the 1.47-V point and below at current densities as high as 50 A/sq ft. Under these conditions, the cell operates "thermoneutrally," and the apparent thermal efficiency is 100%. This gives some confidence that electrolyzer efficiencies approaching 100% can be achieved in practical units. At present, however, operation of the GE cell below 1000 A/sq ft will cause proportionate increases in the effective capital cost, upward from $213/kW. Commercial electrolyzers now cost about $100/kW at 70% efficiency.

Figure A.2-12 represents the cost of hydrogen produced assuming various electrical power costs. In this figure, Stuart and Teledyne costs represent estimates based on actual commercially sold units, whereas GE cell information does not. The data for this figure were obtained individually from each company concerned by specific request of IGT and have not been standardized to a uniform financing method. In other words, it is not certain that the amortization rates, cost of money, return on investment, etc., assumed by each company were the same.

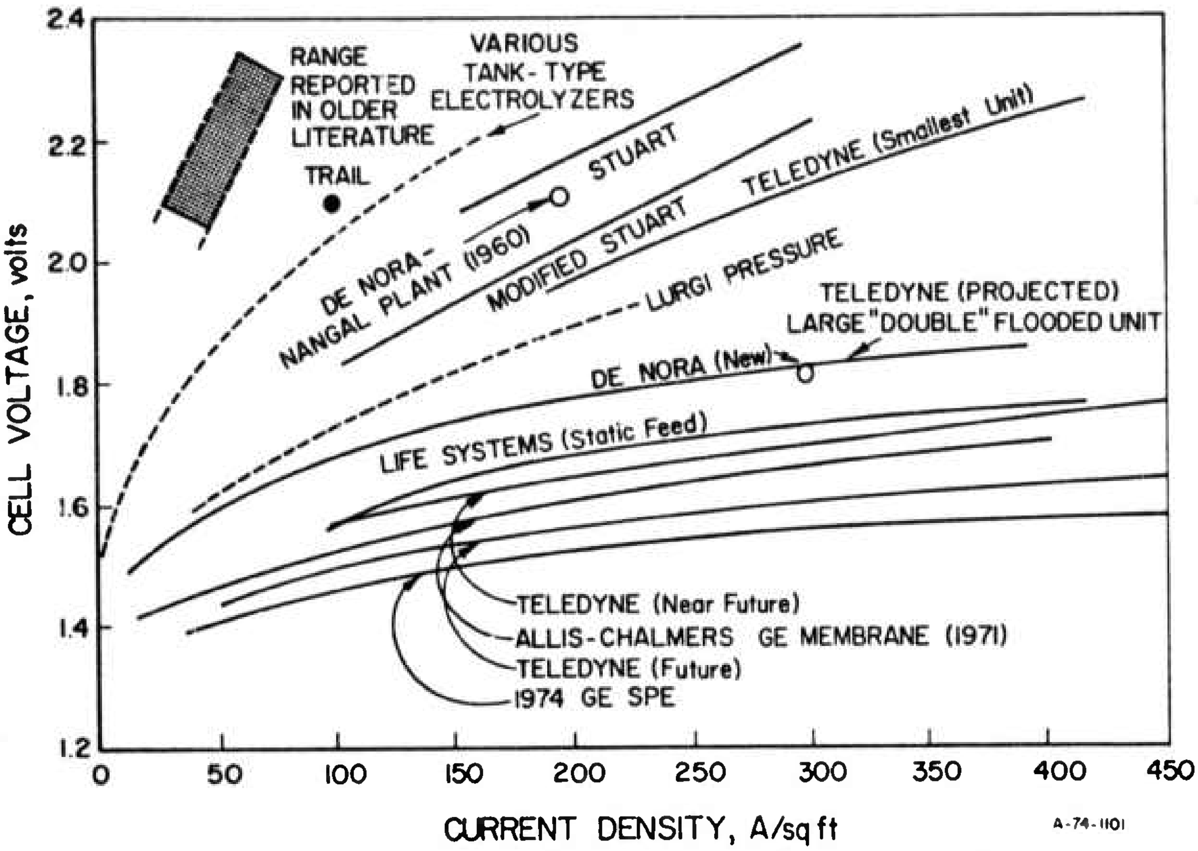


Figure A.2-11: COMPARATIVE PERFORMANCES OF ELECTROLYZER SYSTEMS

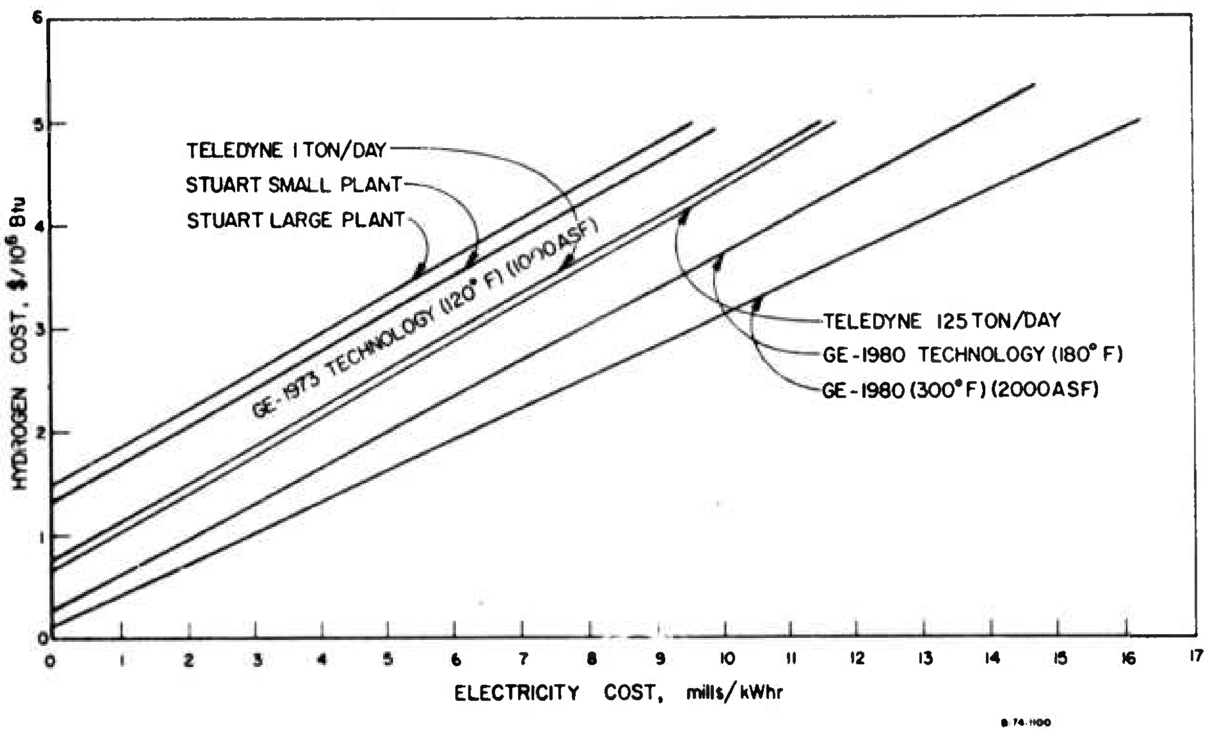


Figure A.2-12: COSTS OF HYDROGEN AS PRODUCED BY VARIOUS PROCESSES

It is not possible to offer definitive comment on the overall merits of the various types of electrolyzer design. Clearly, each approach has its own advocates, and its own merits and problems. It appears likely that several different types of electrolyzers are likely to be developed and used simultaneously. At the present time, among the four large-scale plants, three are of the filter-press type and one is the tank type, none using expensive electrodes. On the other hand, more research effort seems to be, at present, applied to the expensive, sophisticated electrodes than to conventional types.

In the view of De Nora, "tank type cells are obsolete," and "small area cells will never get anywhere commercially." It holds the view that commercial cells can never sustain the cost of porous electrodes, precious-metal catalysts, or sophisticated diaphragms. On the other hand, Electrolyser Corp. regards the tank-type cell as a robust, reliable, and profit-making commercial unit, but shares the view that only the cheapest and simplest electrodes and diaphragms can be tolerated. In direct contrast is the approach of Teledyne, which considers the advantages of controlled pore-size porous-metal electrodes to be worth the extra cost, GE believes that not only the use of platinum catalysts but also of a considerably more expensive electrolyte, the SPE system, is justified by the higher performance obtained. It may be significant that neither Teledyne nor GE has yet installed any really large plants, but that they share a unique capability of operating at or near 100% electrical efficiency.

Another radical difference in design philosophy is apparent from a casual inspection of the various systems. The commercial units of Electrolyser and De Nora are dominated in size and in technical emphasis by the electrochemical cells themselves, whereas the units of Teledyne, GE, and Life Systems are dominated in size and in technical complexity by their auxiliary pumping, pressure control, electrolyte management, and electronic automation equipment (characteristic of the aerospace industry from which they have developed).

It appears that the various design philosophies could result in hydrogen-generation techniques quite different in concept from each other, yet all of industrial significance in appropriate applications.

A.2.6 Ultimate Potential

Present and future overall efficiencies of various electrolyzer cells are given in Table A.2-1.

A.2.7 Research and Development Requirements — Engineering Problems

A.2.7.1 Stuart Cell

According to A.K. Stuart of Electrolyser Corp., both cell improvements and total hydrogen plant development are necessary to improve Stuart cell hydrogen production. An increase in cell operating temperatures (2-year goal) from the current 158°F to 194°F is expected to increase the overall thermal efficiency by lowering the operating voltage. Stuart's 2-3 year goals for electrolyser development include 22.9 kWhr/lb of hydrogen produced, an operating voltage of 1.9, and a thermal efficiency of 77%.[27]

Stuart feels some exploration of advanced diaphragm materials will be necessary to handle the higher temperatures of operation. Present asbestos diaphragms can possibly handle these temperatures, but the upper limits consistent with satisfactory life are not yet known. Life testing is being carried out now. Additional electrode development has the potential to lower cell overvoltage.[27]

Some scale-up of present cells is expected, as mentioned in Stuart electrolyzer technology; however, overall plant development is needed to provide the best economics. The economic conversion of shaft power to high d-c current is considered by Stuart to provide the best opportunity for improved future operation of his cells. Acyclic generators rated at 250,000 A dc would be connected directly to high-current cells. Acyclic generators would not require the switchgear or transformers needed with the more conventional ac-dc rectification equipment. The capital costs for conventional ac-dc conversion are approximately $40/kW whereas capital costs for an acyclic generator are expected to be about $10/kW.[27]

Table A.2-1: PRESENT AND FUTURE COMPARISON OF OVERALL EFFICIENCIES OF VARIOUS ELECTROLYZER CELLS

Manufacturer	Presently Available Potential			2-5 Year Projection Potential			Future (Ultimate) Potential		
	kWhr/lb	V	%*	kWhr/lb	V	%	kWhr/lb	V	%
Teledyne	32	2.1	75	22-19	1.8-1.6	82-92	15	1.24	118
General Electric	22	2.0	74	18-22	1.5-1.8	98-82	15	1.24	118
Stuart	24.5	2.04	72	22.8	1.9	77	--	--	--
Life Systems	20.5	1.7	87	18.1	1.5	98	14.96	1.24	119.8
De Nora	--	1.85	80	--	1.8	82	--	--	--

* % efficiency defined by $\frac{\text{higher heating value of hydrogen produced}}{\text{electrical energy consumed}} \times 100.$

According to Stuart, no heat-transfer problem is expected when his cells operate from a 250,000-A dc source. Heat transfer associated with Stuart-cell scale-up has not posed any problem in a series of scale-ups. Stuart cells operate at a current density of 125 A/sq ft and have gone up to 500 A/sq ft without evident heat difficulty.[27]

A.2.7.2 Teledyne Electra Cell

Future expectations for 2-5 year developments include electrolyzer cells consuming 22-19 kWhr/lb at an operating voltage between 1.8 and 1.6 and an overall thermal efficiency between 82-92%. Ultimate goals project the development of a cell consuming 15 kWhr/lb of hydrogen having an operating voltage of 1.24 at 118% thermal efficiency, which is almost congruous with the thermodynamic limit.[13]

Teledyne mentions certain goals to be attained for the future. Increased operating efficiencies can be achieved by the use of noble-metal catalysts on the electrodes in the modules, but in some cases the additional increase in capital costs can more than offset any advantage gained. Teledyne is presently engaged in continuing the development of low-cost catalysts that would lower overvoltages.

Mr. Kincaide of Teledyne mentions that improvements in cell operating temperature capability are expected within the next 2 years and should produce operating efficiency improvements of 15%. Along with temperature, improvements in cell materials must be developed to withstand the increased temperatures. It is expected that present asbestos diaphragms or gas separators will not be able to withstand increased temperatures of operation, and research is being undertaken to alleviate this problem.

Teledyne revealed that it has had problems in obtaining good commercially manufactured parts for its electrolyzers. In many instances it has developed its own system parts to meet close tolerances and specifications.

All Teledyne systems presently operate at pressures higher than ambient. An insignificant power penalty (0.431 kWhr/lb of hydrogen at 100 psia) is realized when compared with conventional compressors. Teledyne realizes the importance of generating hydrogen at high pressure when storing and transmitting large amounts of the gas.[14] Present systems are limited in their operating pressures by structural features. One specific question being reviewed by Teledyne is that "Does one design a cell stack to withstand pressure or should a pressurized tank be placed around an existing stack?" Studies are being performed to determine the demand and cost effectiveness of high-pressure systems in commercial applications.[13] Teledyne is building electrolytic gas generators for the U.S. Navy that operate at pressures up to 3000 psig. Power penalties for generating gas directly at this pressure are less than 1.197 kWhr/lb.

A.2.7.3 GE Solid Polymer Electrolyte

The future of the GE cell seems to lie in operations at very high efficiencies, or else at very high current densities, thus reducing power costs to a minimum, making the relatively high capital costs justifiable in giving a high hydrogen-production rate. Since these cells will also operate at higher current densities, a greater hydrogen-production rate is realized per unit area of floor space required. It is GE's objective to further improve the thermal efficiency of the SPE cell system and to develop lower cost materials and manufacturing processes in order to achieve a cost for large-scale production of electrolytic hydrogen of \$2-\$3/million Btu (1974 cost basis), assuming electrical power costs in the range of 5-10 mils/kWhr.

Mr. Titterington lists four specific elements to be included in a long-range development program: 1) electrolysis module development, 2) system definition, 3) 5-MW prototype demonstration, and 4) incorporation of advanced technology.

The SPE electrolysis module technology is limited mainly by the cell operating temperature and lack of suitable cell-component materials. The temperature effect on electrolysis cells is shown in Figure A.2-13.[31]

The importance of cell operating temperature is reflected by the fact that an increase in temperature from 80° to 220°F decreases power consumption by 10% for the same amount of hydrogen produced. If cell operating temperatures as high as 300°F can be reached, the theoretical decomposition voltage of water decreases from 1.18 V at 180°F to 1.12 V. It is anticipated that at 300°F, the cell sealing techniques or gasket material may become a problem since they cannot withstand high temperatures and wet environments. Titterington mentioned that newly developed fluorosilicone rubbers would be evaluate for this application. If these are not compatible, sealing concepts that utilize the SPE directly as a gasket-type seal would be developed.

Experience has also been obtained at gas-generation pressures up to 3000 psia, with the resulting effect on performance shown in Figure A.2-14.

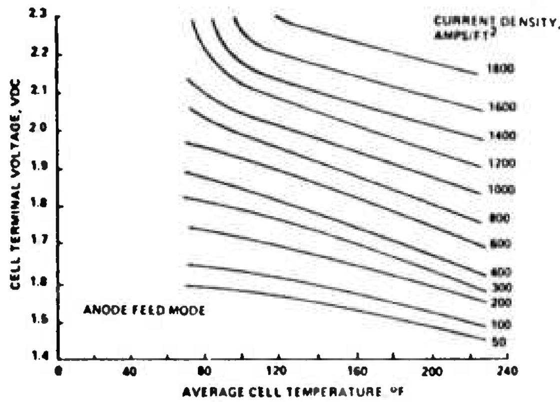


Figure A.2-13: PRESENT SPE WATER ELECTROLYSIS PERFORMANCE CAPABILITY AT AMBIENT CELL PRESSURE

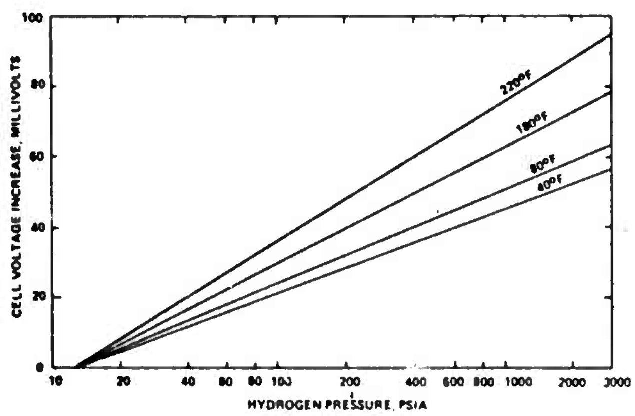


Figure A.2-14: EFFECT OF HYDROGEN PRESSURE ON GE CELL VOLTAGE

Thus, considering a cell that has a voltage of 1.85 V dc at 1000 A/SF, 180°F, and 15 psia gas pressure, the performance would decrease to 1.90 V dc at a hydrogen-generating pressure of 400 psia. This must be taken into consideration in the system power trade-off studies requiring high-pressure operation.

To date, the SPE electrolysis systems have used niobium or titanium as the collector of separator-sheet materials, in spite of statements that the SPE is noncorrosive. Niobium is quite expensive, at $40-$50/lb; titanium, however, offers a desirable price of $8/lb. Cell operation at 300°F may result in hydrogen-embrittlement problems with titanium.[10] Therefore, Titterington states that alternative materials including molybdenum, zirconium, and various alloys of these materials should be tested for compatibility in high-temperature SPE electrolysis.

The present SPE is 12 mils thick in the currently manufactured cells. Considerable voltage reductions could be attained by cutting the present thickness in half. Titterington suggests that minor modifications in both the cell-fabrication technique and hardware design would be required. It is expected that even thinner SPE's could further lower the electrical resistances, and more experimentation is to be conducted. It must also be remembered that as SPE thickness is decreased, its cost is also proportionately decreased. Thus, a 6-mil SPE has a projected cost of $5/sq ft versus the $10/sq ft for a 12-mil SPE. Alternative lower cost SPE's are currently under development and offer costs as low as $2/sq ft.

Two other areas of research that may provide future economic advantages for the SPE cell are lessening of catalyst loadings on the electrodes and the advancement of catalytic electrodes. Progress in these areas could result in lower capital costs for the entire cell and lower overvoltages at both the anode and the cathode. The present cathode catalyst is platinum black with loadings of 4 mg/sq cm. A proprietary metal-alloy catalyst is applied to the anode, also at a loading of 4 mg/sq cm. Expectations of catalyst loadings on both electrodes as low as 1 mg/sq cm are conceivable. Further studies should be carried out to determine the mechanisms of the catalytic activity and the dependence of this activity on catalyst geometry and reactions between a catalyst and its environment.

Mr. Titterington suggests that, before larger electrolytic plants are designed, life tests on cell components and a total analysis of a water electrolysis plant must be carried out to optimize the overall plant system relative to hydrogen production costs, plant safety, reliability, and life.

GE proposes a 5-MW prototype SPE water-electrolysis system to be fabricated and evaluated over a 2-year period. Preliminary calculations have shown that approximately 2500 sq ft of cell will be required for this plant and that it will generate 250 lb/hr of hydrogen.[33]

GE estimates that a 5-MW unit could be built today with no additional research; however, it would have a capital cost of \$560/kW. Capital costs, provided scale-up and cell improvement programs are funded, could be reduced to \$56/kW by 1980 and to \$44/kW by 1985.[33]

Power requirements, operating voltages, and thermal efficiencies for GE's electrolysis cells are 18-22 kWhr/lb, 1.5-1.8 V, and 98-82% for 2-5 year goals, and 15 kWhr/lb, 1.24 V, and 118% for ultimate development.[33]

A.2.7.4 Life Systems' Cell

Life Systems' cells projected capabilities for 1975 are —

Maximum Pressure	2000 psi
Maximum Temperature	300^{0}F — short periods
Maximum Current Density	1500 A/SF
Power Requirement	129 kWhr/1000 SCF of hydrogen at 1500 A/SF
Single-Cell Area	0.10 sq ft

Studies are under way at Life Systems to evaluate an alternative diaphragm material suited for high-temperature ($>200^{0}$F) electrolysis. Potassium titanate has shown some excellent high-temperature and long-life stability capabilities. Additional studies are also being conducted to investigate the availability of alternative structural materials suited for high-temperature applications to enable cell operation with lower electrolysis power requirements. Advanced designs, using zirconia and yttria-thoria ceramics for solid electrolytes are being evaluated. These electrolytes conduct only at temperatures above about 1490^{0}F. Advanced catalyst development is also being performed to increase electrode performance and lower costs. This work is being conducted in parallel with the high-temperature research to develop high-pressure, large-scale hydrogen generation.[10]

In designing its larger electrolysis schemes, Life Systems speculates that many smaller cells connected in series may be more economically and technically feasible than a smaller group of larger cells. R. Wynveen of Life Systems suggests that effective current distribution over large electrode areas (4 x 4 feet) would present design problems, including heat removal.[35] This opinion is in direct conflict with that of Mr. Trisoglio of De Nora, who believes that large single cells of 5 or 6 sq m are essential.

A.2.7.5 Acyclic Generators

In the detailed design of a large hydrogen-generation plant, not only is the electrolysis cell itself an important system-design feature, but d-c generation costs must also be evaluated and optimized.

The acyclic generator, also known as "unipolar" or "homopolar," has emerged as a newly designed modern machine with great promise for industrial use. Its basic principle of operation is not new, but the techniques of machine construction that now provide a highly efficient and reliable generator are significant. This machine is able to generate noncyclic voltage, resulting in pure direct current available at the terminals.

The development of liquid-metal current collectors has been the feature in converting the acyclic generator from an impractical and inefficient machine to the very practical and very efficient machine it is now. Overall energy efficiencies have been raised from 75% to 98%, with a current rating of 250,000 A.

A high-speed acyclic generator with liquid-metal collectors has been developed by GE. Four large units have been in service at the Arnold Engineering Development Center in Tennessee for over 12 years. A much smaller unit is installed at Argonne National Laboratory, Chicago, capable of about 20,000 A at 5 V continuous.

The acyclic generator is limited on available rating variations. The optimum speed, voltage, and ampere ratings are held in fixed relationship. This limitation has been the major barrier to date in industrial applications of the acyclic generator. The economic evaluation frequently becomes unfavorable when the application requirements do not match the acyclic generator capability.

Several recent cost estimates have been obtained from GE for generators in terms of 50 and 100-MW capacities[5]:

	Generator	
	Up to 50 MW	100 MW
	$/kW	
ac	10	10
ac-dc Converter	60 30	30-50 25
d-c Acyclic Generator	9	7

From these figures, it can be seen that the cost of a-c generators plus converters range over the unit size from $40 to $35 kW, whereas the d-c acyclic generator costs $9-$7/kW, for a saving of $31-$28/kW. This is a significant amount when compared with the estimate of $40-$50/kW for the entire electrolyzer at the 1000-MW size.

In view of these advantages, the acyclic generator should be an integral part of electrolytic hydrogen production. However, Mr. Trisoglio of De Nora claims to have studied the application of acyclic generators for water electrolysis and for other electrochemical applications and has concluded that the additional costs of bus bars and other equipment needed to use these low-voltage generators is in fact greater than the cost of rectifiers for a-c use. This result was obtained in a system study for a 550,000-A unit, with cell stacks operating at generator voltages of 2 V or so for acyclics and 600 V or so for ac-dc rectifiers. De Nora's opinion itself is in direct contrast with that of the Electrolyser Corp., although at this time, no major electrochemical plant has ever been constructed to operate from acyclic generators.

A.2.8. References Cited

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A.3 - PRODUCTION OF HYDROGEN BY COAL GASIFICATION

A.3.1 - Introduction

There are a number of processes by which hydrogen may be generated. The particular hydrogen generation process which is used in any installation depends on the quantity of hydrogen needed, the price and the availability of feed stocks and the price of power currently in the United States. For small scale generation of hydrogen (up to 200 cubic feet per day), the electrolytic method is most convenient, even if the price of electricity is high. In the intermediate range (200-20,000 CF/D), the cracking of ammonia is a very practical method, if the presence of nitrogen is not objectionable. In larger capacity applications, hydrogen is now most economically made by steam reforming of natural gas or naphtha.

The purity of the hydrogen generated from natural gas or naphtha is generally in the 95-98 percent range if CO_2 removal is accomplished by MEA scrubbing. By the addition of pressure swing adsorption units, a methanation reactor, or with cryogenic upgrading, hydrogen purity of 99.999 percent can be achieved (Ref. 1,2).

There are a number of uses which require large quantities of hydrogen. The principal large users are the ammonia synthesis plants. This is followed by the petroleum refining operations such as hydrogenation, hydro-desulfurization, hydrocracking, etc.

The first synthetic ammonia plant in 1913 used hydrogen generated from coal. Coal remained the principal starting material for hydrogen until the late 1940's. Despite the recently tripled price of naphtha, the reverse trend to coal has not yet occurred (see Table A.3-1) (Ref. 3,4,5).

A.3.1.1 - Historical Background

The conversion of coal to gas originated in the late 18th century. Coal was gasified by heating it in the absence of air. The gas produced was called coal gas. The first coal gas company in the United States was chartered in 1816. The primary goal

TABLE A.3-1 -LIST OF HYDROGEN PLANTS UNDER CONSTRUCTION *

COMPANY	PLANT SITE	PROJECT	CAPACITY	ESTIMATED COST MM$	STATUS	LICENSOR	ENGINEERING	CONTRACTORS
Standard Oil Co. Calif.	Richmond, Calif.	Hydrogen	-	-	E 75	KTI	BRAUN	BRAUN
Murphy Oil Co.	Meraux, Lousiana	Hydrogen	40.0 MM CF/D	-	E 76	-	PARSONS RM	PARSONS RM
Koch Rfg.Co.	Pine Bend, Minn.	Hydrogen	-	15.0	U 74	-	PARSONS RM	PARSONS RM
Standard Oil Co. Calif.	Perth Amboy, N.J.	Hydrogen	-	-	P 75	-	FW	FW
Shell Chemical Co.	Marietta, Ohio	Hydrogen	.5 MM CF/D	-	U	HOWE - BAKER	HOWE-BAKER	BLAW-KNOX
Irving RFG. Ltd.	Saint John New Brunswick, Can.	Hydrogen	-	-	U 73	-	FW	FW
Petroquim Gen. Mosconi	Ensenada (Argen-(tina	Hydrogen	38.5 T/D	60.0	U 74	GERMAN LINDE	GERMAN LINDE	McKEE
Bahamas Dir Rfg. Co.	Freeport, Bahamas	Hydrogen	25.0 MM CF/D	-	U 74	-	BADGER	BADGER
Petr. Brasil SA	Salvador Brazil	Hydrogen	1.0 MM CF/D	17.5	U 74	-	FW	-
Petr. Brasiliero	San Jose Campos, Brazil	Hydrogen	12.0 MM CF/D	180	E 77	-	SNAM PROGGETT	SNAM PROGGETT
Empresa Columbiana	Barranca-Beameja, Colombia	Hydrogen	14.0 MM CF/D	-	P 76	-	-	-

MPANY	PLANT SITE	PROJECT	CAPACITY	ESTIMATED COST MM$	STATUS	LICENSOR	ENGINEERING	CONTRACTORS
St.Croix Petro-chemical Corp.	St.Croix Virgin Islands	Hydrogen	5.7 MM CF/D	-	E 74	-	HOWE-BAKER	FLUOR
Ind. Siciliana Asfalti B	Siracusa, Italy	Hydrogen	18.3 MM CF/D	-	U 74	ERECO	SNAM PROGETT	SNAM PROGETT
Empresa Natl. Petr. Tarrag	Tarra-gona (Spain)	Hydrogen	10.0 MM CF/D	-	U 75	UOP	TECNICA REU	STAFF
Tech Mash-Import	Lenngrad (USSR)	Hydrogen	6.0 MM CF/D	1.2	E 75	HRI	HRI TECH SER /KAWASAKI	KAWASAKI
Wintershall AG Erdol Rfy.	Salzbergen (W.Germany)	Hydrogen	-	-	U	KTI	-	KTI
Natl. Iranian Oil Co.	Tehran (Iran)	Hydrogen	33.0 MM CF/D	-	E 76	UOP	SNAM PROGETT	SNAM PROGETT
Natl. Iranian Oil Co.	Tehran (Iran)	Hydrogen	30.5 MM CF/D	-	U 75	-	FLUOR	FLUOR
Riyadh Rfy.	Riyadh (Saudi Arabia)	Hydrogen	15.4 MM CF/D	-	U 74	UOP	CHIYOPA	CHIYOPA
China Natl. Tech. Import	Sheng Yang, China	Hydrogen	4.5 MM CF/D	-	P 77	TECHNIP	SPEICHIN/ TECHNIF	SPEICHIM/ TECHNIP

COMPANY	PLANT SITE	PROJECT	CAPACITY	ESTIMATED COST MM$	STATUS	LICENSOR	ENGINEERING	CONTRACTORS
Asia Kyoseki Co. Ltd.	Sakaide (Japan)	Hydrogen	22.4 MM CF/D	-	E 75	TOPSOE	CHIYODA	CHIYODA
Asia Kyoseki Co.Ltd.	Sakaide (Japan)	Hydrogen	-	-	P	-	-	-
Fuji Oil Co. Ltd.	Chiba	Hydrogen	19.0 MM CF/D	-	U 77	TOPSOE	CHIYODA	CHIYODA
Idemitsu Kosan Co. Ltd.	Aichi (Japan)	Hydrogen	61.6 MM CF/D	-	U 75	TOPSOE	CHIYODA	CHIYODA
Idemitsu Kosan Co. Ltd.	Tokuyama (Japan)	Hydrogen	15.0 MM CF/D	-	U 74	ICI	IHI	ICI
Idemitsu Kosan Co. Ltd.	Tokuyama (Japan)	Hydrogen	19.0 MM CF/D	-	U 75	ICI	IHI	IHI
Mitsubishi Oil Co. Ltd.	Mizushima (Japan)	Hydrogen	39.0 MM CF/D	-	U 74	TOPSOE	CHIYODA	CHIYODA
Nihon Kai Oil Co. Ltd.	Toyama (Japan)	Hydrogen	50.0 MM CF/D	-	P 77	-	-	-
Nippon Mining Co. Ltd.	Mizushima (Japan)	Hydrogen	29.0 MM CF/D	-	E 74	TOPSOE	CHIYODA	CHIYODA
Chinese Petr.	Hsin Chu Kadhsiung Taiwan	Hydrogen	50.0 MM CF/D	-	U 74	TOPSOE	PARSONS RM	PARSONS RM
Western Mining Corp.	Kwinana (Australia)	Hydrogen	2.4 MM CF/D	-	E 74	HOWE-BAKER	HOWE-BAKER	AAEC/ WOODALL-D

MPANY	PLANT SITE	PROJECT	CAPACITY	ESTIMATED COST MM$	STATUS	LICENSOR	ENGINEERING	CONTRACTOR
Shell Oil Co.	Norco, Louisi-ana	Hydrogen	2.0 MM CF/D	-	U 74	HOWE-BAKER	HOWE-BAKER	KELLOGG
Basf Ag	Ludwig-shaffen W.Ger-many	Hydrogen	7.0 T/D	-	U 74	GERMAN-LINDE	GERMAN-LINDE	GERMAN-LINDE
Bayer Ag	Bruns-buttel W.Ger-many	Hydrogen	-	-	U 75	GERMAN-LINDE	GERMAN-LINDE	GERMAN-LINDE
Jeddah Oil Rfy.	Jeddah (Saudi Arabia)	Hydrogen	6.7 MM CF/D	-	U 74	UOP	CHIYODA	CHIYODA
Asia Oil Co.	Yoko-hama, Japan	Hydrogen	28.0 MM CF/D	-	E 75	BENFIELD/ ICI	DPT LTD/ MKK	MKK
Fujo Oil Co. Ltd.	Chiba, Japan	Hydrogen	19.0 MM CF/D	-	U 75	TOPSOE	CHIYODA	CHIYODA
Korea Ind, Equipment	Puyang-Tang, North Korea	Hydrogen	7.0 T/D	-	U 74	GERMAN-LINDE	GERMAN-LINDE	SPEICHIM

* Of the 38 plants listed above, 35 currently plan to use petroleum products as a feedstock.

KEY

MMCF/D	=	MILLIONS OF CUBIC FEET PER DAY
T/D	=	LONG TONS PER DAY
MMCF/Y	=	MILLIONS OF CUBIC FEET PER YEAR

STATUS

P = PLANNING

E = ENGINEERING

U = UNDER CONSTRUCTION

C = COMPLETED = DELETED FROM SUBSEQUENT TABULATIONS

76 = LAST TWO NUMBERS OF YEAR OF ESTIMATED COMPLETION

REFERENCES - TABLES A.3-1, A.3-2 and A.3-3 obtained from:

1. HYDROCARBON PROCESSING (SECTION 2) Pg. 1-39 JUNE 1974
2. Mr. John Gallagher, American Lurgi, New York

of coal to gas conversion was the production of gas which could be used for lighting purposes. In the coal gas production, about 2/3 of the original coal was not utilized, and the remaining carbon and ash residue was sold or burned in the plant elsewhere (Ref. 7).

A gas similar in composition to the coal gas is produced when coal is heated in the manufacture of coke. Frequently, the coke oven gas was used to supplement coal gas when it was locally available. In the coke oven gas production, there was no low priced by-product since the remaining solid carbon (coke) was used in the production of steel or cast iron. Typical heating values of coal gas and of coke oven gas ranged from 475 to 575 BTU/CF.

A third process of coal gasification was developed in the middle 1800's. This process was the producer gas manufacturing method in which dry air was blown through a bed of coke or coal of sufficient depth to produce a combustible gas consisting primarily of carbon monoxide and nitrogen at a ratio of about 1 to 2. The heating value of the gas from early producers was only from 100-130 BTU/CF.

The heat liberated in the process of producing this gas was much greater than that required to maintain the fuel bed at the desired temperature. As a result, an undesirable side effect was often the formation of fused ash (clinker) in the fuel bed which complicated the operations of the gas producer. Also, much of the potential heat in the fuel left the producer as sensible heat in the gas, and unless the producer gas was used in the plant itself much of the sensible heat was lost.

To increase the thermal efficiency and to moderate the temperature of the fuel bed, steam was introduced to the blast. This resulted in additional generation of fuel gas by the reaction of carbon with steam. The reaction, being endothermic, had the effect of reducing the fuel bed temperature and preventing the fusing of the ash.

Typical heating value of producer gas made with air-steam

blasting was from 130 to 160 BTU/CF. The composition of the gas was about 50 percent nitrogen, 25 percent carbon monoxide, 15 percent hydrogen, the remainder being carbon dioxide, methane, etc.

Since the heating values of carbon monoxide and of hydrogen are only 320 and 310 BTU/CF, respectively, and in order to raise the heating value of the producer gas, nitrogen had to be excluded from the process. This was achieved by two methods. The first method involved the alternate preheating of coke by combusting it with air, followed by the generation of a combustible gas using steam only. The second approach involved the use of oxygen rather than air in the gas generation process.

In the late nineteenth century the blue gas process was developed in which steam was passed over red hot carbon at a temperature from 1750^{o} - 2200^{o}F. The gas thus formed burned with a non-luminous bluish flame and for this reason it was called "blue gas" or "blue water gas". Since the basic reaction to produce the blue gas (90 percent of which is carbon monoxide and hydrogen in a proportion of about 1 to 1) is endothermic, the temperature of the fuel bed has to be raised periodically from 1750F to 2200 F. This was done by blasting air through the carbon bed raising its temperature to the desired level After the "blow" period, the air valves were shut off and steam was again passed through the carbon bed generating the blue gas. The heating value of the "blue gas" was about 300 BTU/CF.

Most of the town gases distributed throughout the United States cities prior to 1945 had a heating value between 450 and 500 BTU/CF. The blue gas was usually enriched by the addition of light hydrocarbons produced during thermal cracking of heavy fuel oil sprayed on hot bricks.

In the early 1920's the use of oxygen and steam (rather than air and steam) was first introduced for coal gasification on a commercial scale in the Winkler process. The Winkler coal gasifier is a fluidized bed reactor which operates at near atmospheric con-

dition.

The second process to use oxygen and steam to produce gas from coal is the Lurgi process, commercially introduced in the 1930's. The Lurgi counter current flow shaft gasifier operates at a pressure from 300 to 400 psi and rejects essentially a carbon free ash (Ref. 8).

The third process to use oxygen and steam for coal gasification was the Koppers-Totzek process first tested in 1948. The Koppers-Totzek reactor is a partial pulverized coal combustor operated at near atmospheric conditions (Ref. 9,10).

Currently there are no Winkler, Lurgi or Koppers-Totzek gasifiers operating in the United States. Five Lurgi technology plants for the United States are in engineering study stages, and when built will be used to supply hydrogen and carbon monoxide for the production of methane (natural gas).

In recent years many more coal gasification processes have been proposed and are at different stages of development. None of the new processes, however, are producing gas on a commercial scale (Ref. 11).

A.3.2 - Gasification Reactions for Production of Hydrogen

All fossil fuel gasification processes produce a gas that is essentially a mixture of hydrogen and carbon oxides with widely different admixtures of nitrogen, steam, hydrogen sulfide, ammonia, methane, other hydrocarbons and other gases.

The basic reactions are few and are often identified by a special name.

First, we have the thermal cracking reactions:

for methane: $$CH_4 + \Delta \rightarrow C + 2H_2 \quad (1a)$$

for other hydrocarbons: $$CH_n + \Delta \rightarrow C + \frac{n}{2} H_2 \quad (1b)$$

The reactions take place at a temperature above 1600 F and are used in commercial processes to furnish carbon for rubber manufacture and hydrogen for ammonia synthesis.

Methane in the presence of steam and a catalyst produces hydrogen by the following reaction:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (2a)$$

A similar reaction of carbon with steam is the principal reaction by which blue water gas is made:

$$C + H_2O \rightarrow CO + H_2 \qquad (2b)$$

Carbon is converted to carbon oxides by:

$$2C + O_2 \rightarrow 2CO \qquad (3a)$$

$$C + O_2 \rightarrow CO_2 \qquad (3b)$$

$$2CO + O_2 \rightarrow 2CO_2 \qquad (3c)$$

Reaction (3a) is the principal mechanism of carbon consumption, while (3b) and (3c) are principal exothermic reactions.

The water gas shift reaction is an important method by which hydrogen is adjusted to derived concentrations in the final stream. It is usually carried out in two steps in presence of excess steam.

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (4a)$$

The methanation reaction is used to remove final traces of carbon monoxide from a hydrogen stream when ultra high priority gas is desired, and also is the principal reaction for the production of substitute natural gas (SNG).

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (5a)$$

At one time the steam-iron method of hydrogen production was the basis for an important commercial process (patented 1861), successfully developed about 1900. It is again being seriously looked at for hydrogen production in a continuous process using char (produced in a coal gasification process) for a source of H_2 and CO (Ref. 12).

The original method involved the passing of steam over iron heated to about 1200 F. The reaction proceeded according to the equation:

$$3\ Fe + 4\ H_2O \rightarrow Fe_3O_4 + 4\ H_2 \qquad (6a)$$

After a 10 minute hydrogen generation step, the iron oxide was regenerated during a 20 minute cycle using blue water gas:

$$Fe_3O_4 + 2\ CO + 2H_2 \rightarrow 3Fe_3 + 2\ CO_2 + 2\ H_2O \qquad (6b)$$

About thirty years ago, this process had widespread use in plants hydrogenerating vegetable oils.

A.3.3 - Gas Producers

In its simplest form, a gas producer consists of a vertical brick-lined vessel on top of which is a charging hopper and on the bottom of which is a grate with the air and steam blast distributor plates. A diagrammatic sketch of a gas producer is shown in Figure A.3-1 (Ref. 6).

The fuel bed in the gasifier travels vertically from top to bottom, being consumed in the process of coal gasification. One can divide the bed into a succession of horizontal zones: the ash zone, the combustion (or oxidation) zone, the reduction zone, and the distillation zone.

a). The ash zone - extends from the grate upward toward a carbon combustion zone. Air and steam enter as uniformly as possibly over the whole section and move upward through the bed. The air and steam cooled ash is removed by continuously rotating or intermittently moving the grate. Any clinker formed earlier is crushed. The ash is usually dropped into water-sealed troughs. For proper operation, it is most important that the blast distribution is uniform, that no gas channeling occurs, that no significant quantities of carbon remain and that the ash does not fuse.

b). The combustion zone - occupies a rather thin (about six inches thick) region in which oxygen reacts with carbon in the fuel. The temperature of this zone may reach about 3000 F. In the bottom of the zone the carbon oxidation product is primarily carbon dioxide. Near the top of this zone carbon monoxide is formed. The temperature must be closely controlled to prevent the formation of large clinker lumps, by the proper propor-

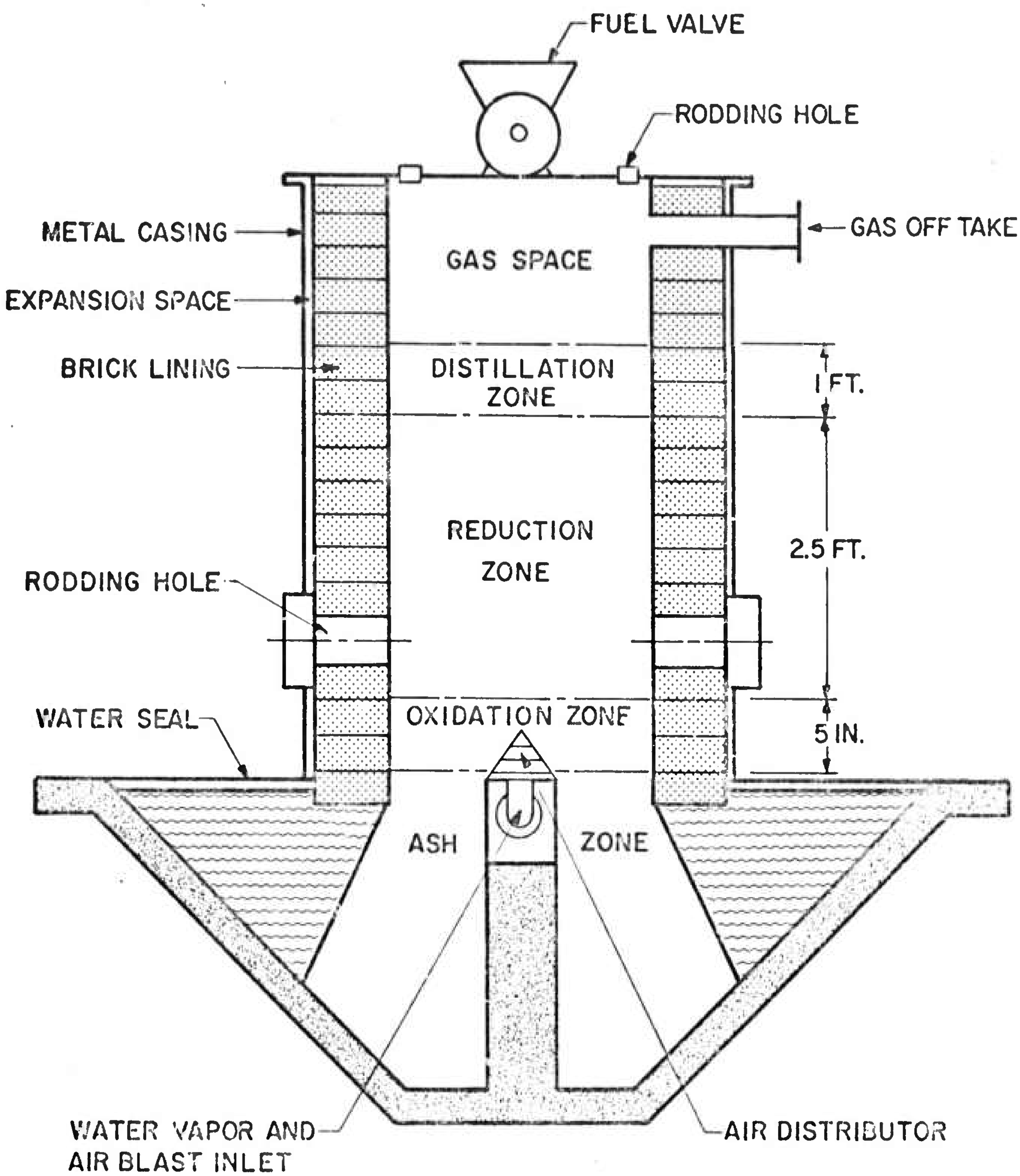

FIGURE A.3-1: DIAGRAMMATIC SKETCH OF A GAS PRODUCER

tioning of steam and air.

c). The reduction zone - extends for a distance from one to five feet, in which the temperature drops from about 2200 F to about 1500 F. Here no significant oxygen remains, most of the carbon dioxide is converted to carbon monoxide and a significant concentration of hydrogen is first noticed. Near the top of the zone no significant gasification of fixed carbon occurs.

d). The distillation zone - is a zone in which the hot gases from below preheat the coal and cause the volatilization and the cracking of the more volatile coal constituents. The character of the products of the distillation zone depends most strongly on the type of coal fed into the gasifier.

The producer gas composition is typically:

Fuel Used	Composition of gas made, vol.%						Caloric Value (Btu/ft^3)
	CO_2	O_2	CO	H_2	CH_4	N_2	
Coke	6.0	-	27.0	12.5	0.6	53.9	132
Coal	6.0	-	26.0	15.0	2.5	50.5	156

In order to increase the concentration of hydrogen in the stream above the 15 percent level, all the gases present in the streams except hydrogen may be adsorbed using the pressure swing adsorption method. Carbon monoxide may then be recovered from the desorbed gas stream by the cryogenic method and then subjected to the "water-gas shift" reaction, forming additional hydrogen. Since for each carbon monoxide molecule one molecule of hydrogen is formed, the total amount of hydrogen that can be recovered from the producer gas is about 40 percent. The maximum volume of hydrogen that can be manufactured by the producer method is approximately 30 standard cubic feet per pound of carbon gasified.

In 1926 coal gasification (using the producer gas method) reached its peak in the United States. Approximately 15 million tons of coal and coke were gasified that year in some 12,000 gas producers, generating about eight billion cubic feet per day of producer gas. The total heating value of this amount of producer gas was equivalent to the use of about 200,000 barrels of crude oil per day.

At present there is only one gas producer still operating in the United States. This is a ten foot diameter Wellman-Galusha generator located at the Glen-Gery Corporation plant in Shoemakersville, Pennsylvania. It produces about 10 million cubic feet/day of gas containing approximately 50 percent nitrogen, 26 percent carbon monoxide, 14 percent hydrogen, and the remainder carbon dioxide, methane and other. At current anthracite prices, including depreciation and maintenance of the producer unit, the gas is produced at a cost of about $1.00 per million Btu's (Ref. 13).

A3.4 - Lurgi Gasifiers

Prior to 1932, all processes for the gasification of coal operated at low pressure (near atmospheric). Through the pioneering work of Lurgi engineers, it was found that, significant reduction in capital and operating costs for the production of town gas from low grade coal could be realized if the coal gasification was conducted at near 400 psi pressure using oxygen rather than air for blasting. (The use of oxygen for gasification was first introduced by Winkler early in the 1920"s).

A typical Lurgi's gasification plant has as its key component the Lurgi Gasifier (Fig. A.3-2). The gasifier is a double walled pressure vessel. The annulus between the walls acts as a steam generator (Ref. 8).

Fuel is charged through a lock hopper and is distributed uniformly throughout the 15 foot diameter bed. The coal lock hopper is operated with two valves. Coal enters from the feeder to the coal lock when the bottom valve on the lock hopper is closed. When the coal lock is filled, the top valve is closed, the coal lock is pressurized and then the lower valve is opened. If the coal tends to cake, a stirrer device is provided. The gas leaves the reactor near the top at temperatures from 700 - 1100 F.

A mixture of oxygen and steam are added through the rotating grate at the bottom of the reactor. Ash is removed through a semi-automatic ash lock using locking and emptying valves similar to those used for coal feeding. Because the process is operated under pressure

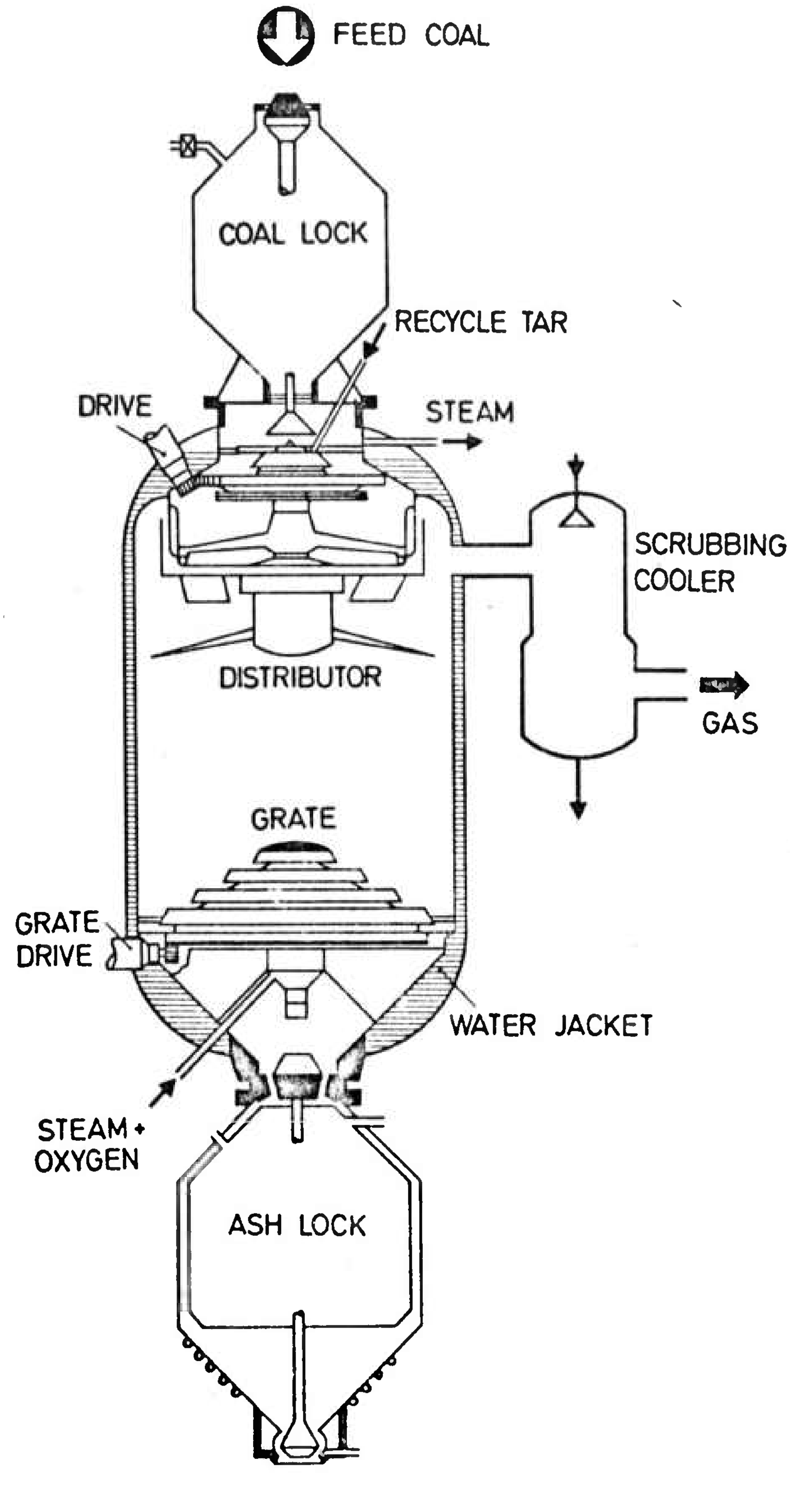

FIGURE A. 3-2: LURGI PRESSURE GASIFIER

it is of utmost importance that no gas leakage through the valves occurs. Although some repairs on the locks can be made while the unit is operating, in general, the reactor must be shut-down if significant wear of the valve has occurred and pressure cannot be maintained. To assure continued operation of the plant, usually for every three gasifiers needed to meet the full production schedule, a fourth unit is added to be ready for emergency operation or for scheduled maintenance. In a proposed SNG Lurgi plant, 30 gasifiers will be used to convert about 22,000 tons of coal per day to produce about 250 million cubic feet of product gas, consisting primarily of methane. An additional 3,000 tons of coal will be used to raise steam and provide electrical power (Ref. 14).

The consumption and production figures associated with the Lurgi Process for different coals are as follows: (per 1000 CF of raw gas produced)

	Feed Material		
Gas Analysis, Vol. % (dry basis)	Lignite	Sub-bituminous coal	Low Volatile coal
CO_2	31.9	28.2	26.5
$C_n H_m$	0.5	0.3	0.1
CO	17.4	20.6	21.4
H_2	36.4	39.6	43.5
CH_4	13.5	10.5	8.0
N_2	0.3	0.8	0.5

	Feed Material		
Feed Streams:	Lignite	Sub-bituminous coal	Low Volatile coal
Coal (lbs.)	41	29	22
O_2 CF	107	140	150
Steam (lbs.)	38	41	44
Feed Water (lbs.)	5	10	13

Compounds, lbs.	Feed Material		
	Lignite	Sub-bituminous coal	Low Volatile coal
Tar, oil, light naphthat, etc.	3.7	2.7	0.25
Ammonia	0.37	0.31	0.025
Water Vapor	33.6	33.7	32.8
Sulfur Compounds	Quantities vary with the sulfur content of coal		

As shown in the table above, raw gas leaving the gasifier is saturated with steam and contains tar, oil, etc. It is possible to reform the heavy hydrocarbon streams by partial oxidation to hydrogen and carbon monoxide. The crude gas can then be subjected to gas shift conversion to convert the carbon monoxide to hydrogen.

Carbon dioxide and the sulfur compounds are removed by Rectisol wash combined with nitrogen wash. If a high degree of hydrogen purity is desired, the gas may be further subjected to methanation or cryogenic upgrading. If ammonia, methanol or synthetic natural gas are the final products, the hydrogen need not be purified further.

Currently, Lurgi's gasifiers are used in some fourteen installations, the oldest one located near Zeitz, Germany which has been in operation since 1936. The total capacity of Lurgi's gasifiers is now 484 MM CF/D. There is a total of fourteen plants now operating world wide. It should be noted that most of the gasifiers are used primarily to supply town gas. Only the David Khel, Pakistan and the Sasolburg, South Africa plants are used for the production of high purity hydrogen from coal which is used in ammonia synthesis, substitute natural gas production, etc.

Five very large Lurgi coal gasification plants, by any standard, each about 250 MMCF/D, are in engineering and planning stages in the United States. They are: the El Paso Natural Gas Company and the Western Gasification plants in New Mexico, and the Panhandle Eastern and the Cities Service-Northern Natural Gas plants in Wyoming and the American Natural Gas plant in North Dakota. The plants are de-

signed to produce substitute natural gas, primarily methane. Although the estimated completion date for the El Paso plant is now 1977, since all the necessary permits have not as yet been obtained and since the reactor vessels have as yet not been ordered, it is doubtful that the first plant can be started up prior to 1978. The total anticipated cost for the five plants is about 2.5 billion dollars (1974 est.) (Ref. 15).

It should be noted, however, that applications for only two plants have been filed at this time with the FPC.

A.3.5 - Koppers-Totzek Gasification Process

The Koppers-Totzek (K-T) process is relatively new. It was first introduced in Germany in 1948 and a year later in the United States, where a pilot plant operated for two years. The first commercial plant was built in Finland in 1952 and presently the process leads in total installed capacity for worldwide coal gasification - 650 MMCF/D (Fig. A.3-3). Since 1952, 85 percent of new synthesis gas capacity via coal gasification has been captured by the K-T process.

The gasifier in the K-T process consists of two (or four) spheroidal cones centrally welded together with one central outlet upward for gas removal and a bottom outlet for slag removal. Double walls are used to provide an annulus for cooling water, and also to generate low pressure steam (Fig. A.3-4).

The burners are located at the apex of each gasifier cone. Each burner is mounted in line with the opposing set. Coal is conveyed to the feed screw conveyors by nitrogen. Oxygen and steam are injected with the coal into the gasifier. The combustion and gasification of coal particles is essentially complete by the time they enter the waste heat boiler. Due to the high temperatures in the gasifier 2700-3500F, essentially all liquid and gaseous hydrocarbons, tars, phenols, ammonia, etc. are dissociated and oxidized. The gas leaving the gasifier is at near equilibrium condition. The gas composition is typically:

CO	- 50%
CO_2	- 5.5%
H_2	- 33%
H_2O	- 10%

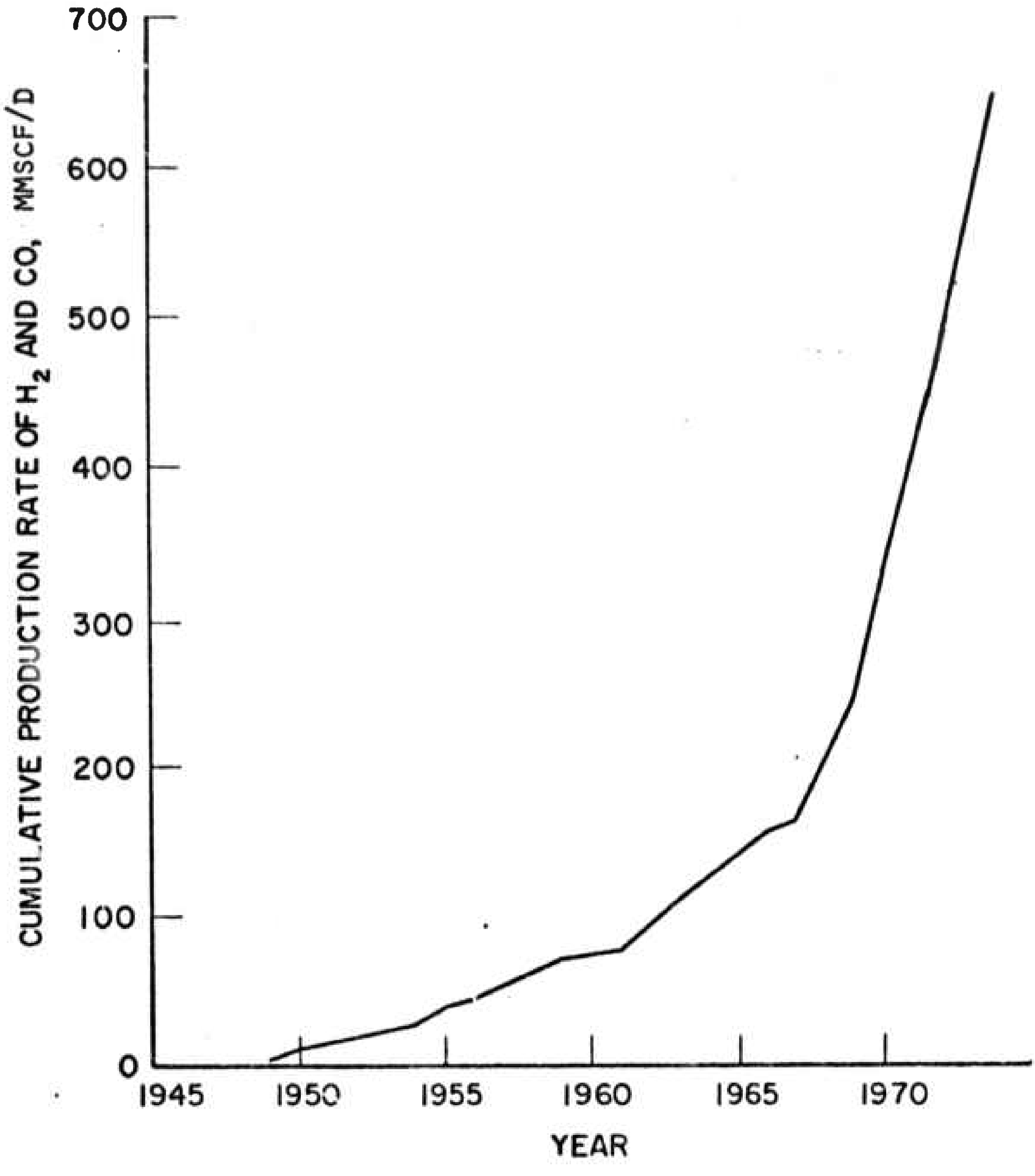

FIGURE A.3-3: GROWTH IN USE OF KOPPERS-TOTZEK PROCESS FOR COAL GASIFICATION

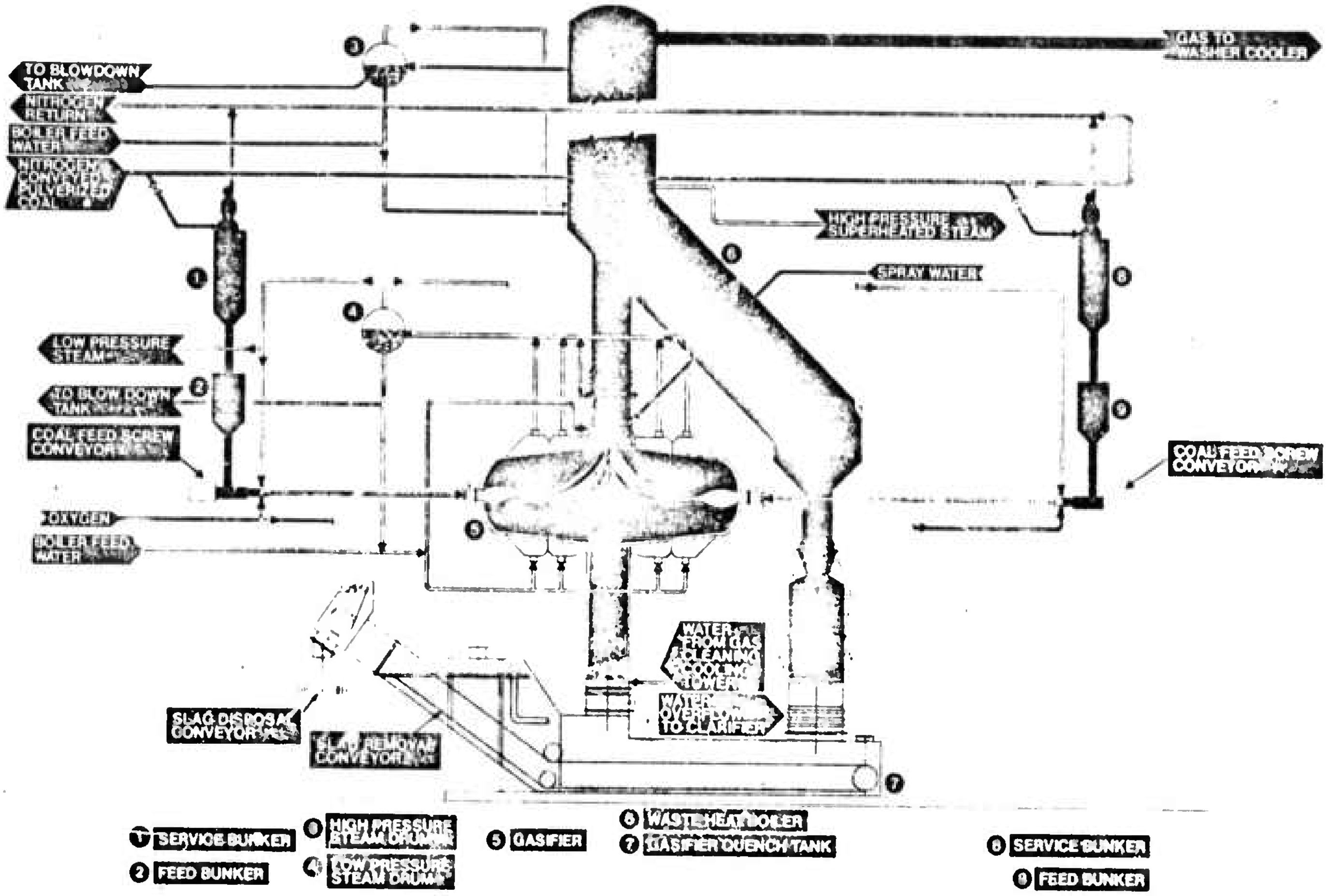

FIGURE A. 3-4: KOPPERS - TOTZEK GASIFICATION PROCESS

and the remainder being nitrogen, hydrogen sulfide, etc.

About half of the ash leaves the bottom of the gasifier as molten slag. The other half leaves the gasifier as fly ash entrained in the raw gas.

The gases are cooled and washed in a vertical spray tower to about 95F. The gas washing is followed by other particulate and hydrogen sulfide removal equipment. The particulate and H_2S-free gases can then be subjected to CO-shift conversion and CO_2 removal to produce either pure hydrogen gas or other H_2 to CO gas combination, depending on what the final gasification and synthesis product is to be.

The largest four headed gasifier constructed to date has a maximum production capability of about 30 MMCF/D of dry gas. Largest two-headed gasifiers have the dry gas production capacity of 20 MMCF/D. Intensive pilot plant work is currently being pursued in Europe to develop a K-T gasifier which would operate at elevated pressures (from 200-400 psi). (Ref. 19). If successful, the improvements in the reduced capital cost and reduced oxygen demand for coal gasification would make the K-T process very attractive for industrial hydrogen production vis-a-vis a liquid hydrocarbon steam reforming process or any of the other coal gasification routes.

A.3.6 - Winkler Gasification Process

The Winkler gasification process was developed during the 1920's in Germany. It was the first process to use oxygen for coal gasification. Typically, the generator is a 60 ft. long x 15 ft. diameter vessel, lined with brick along its entire length. (Fig. A.3-5). It has a grate at the bottom through which 90 percent of the blase oxygen and steam are introduced. A water cooled scraper driven by a rotating shaft transfers the ashes on the grate to an opening to the ash pit from which ashes are removed periodically.

The fluidized bed is from 4 to 8 feet high. Fresh coal is fed from a feed bunker through water-jacketed screw conveyors located about half way up the reactor vessel. The coal is, therefore, par-

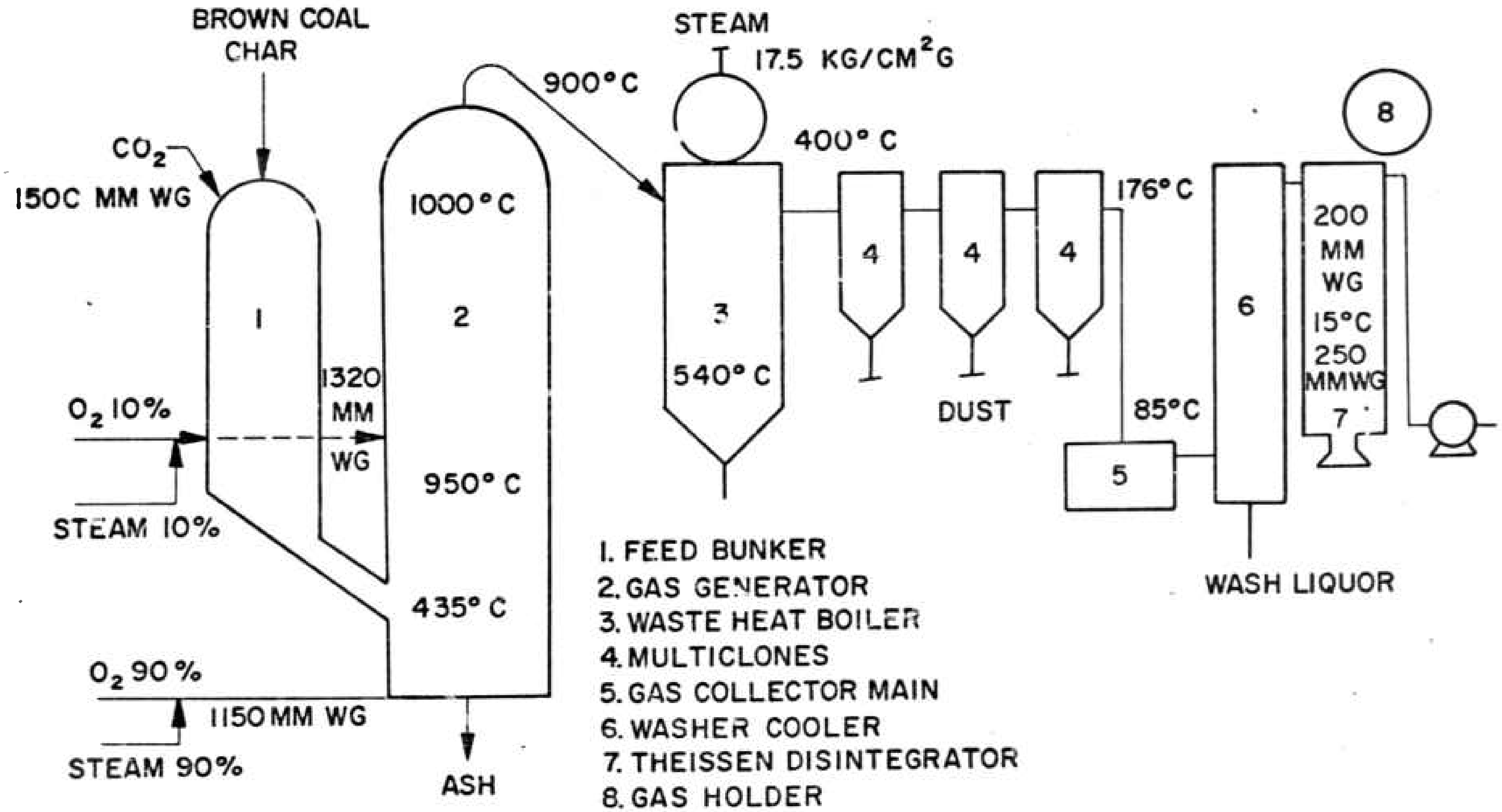

FIGURE A.3-5: FLOW DIAGRAM OF THE WINKLER GASIFICATION PROCESS

tially volatilized and pyrolyzed before it falls into the fluidized bed. Typically, ten percent of the blast oxygen and steam are introduced above the fluidized bed to promote the volatilization and pyrolysis process above the fluidized bed.

The sensible heat in the gas is recovered by generating steam. Because of the heavy dust and unburned coal loading in the effluent gas stream, cyclone collectors are added prior to the boiler tubes. The collected dry overhead dust may be reused in a service boiler for raising steam or for pre-drying of coal. A typical analysis of the overhead dust may contain up to 50 percent of the carbon fed to the reactor.

The composition of a typical gas from lignite gasified in a Winkler generator, falls into the following ranges on dry basis:

CO_2	-	16 - 24%
H_2	-	38 - 44%
CO	-	27 - 42%
N_2	-	0.5 - 1.5%
CH_4	-	0.7 - 1.5%
H_2S	-	0.5 - 1.5%

The raw gas must be cleaned by similar processes as used in the Lurgi gasification plants.

There are 36 Winkler gasifiers in existence today. The feed to the Winkler unit must be a non-caking coal. Lignite or low rank coals are typically used.

If it is desired to eliminate significant production of methane, tars or lighter distillates, tuyeres are arranged above the fluidized bed and additional steam and oxygen are injected into the steam.

The control of the coal particle diameter is not as critical as it is for the Lurgi process, however, the presence of too many fires results in poor coal utilization efficiency.

A.3.7 - Other Coal Gasification Processes

Currently there are four additional coal gasification projects in the United States at various advanced pilot plant stages of development. They are:

1. Hygas (IGT/AGA), 75 T/D pilot plant operating
2. CO_2 Acceptor (Consolidation Coal), 40 T/D pilot plant operating
3. Synthane (Bureau of Mines), 70 T/D pilot plant completed.
4. Bi-Gas (Bituminous Coal Research), 120 T/D pilot plant under construction

In addition to this there is one pilot plant under construction to produce hydrogen gas by a modified steam-iron method in which the iron oxide is regenerated using the coal char from the Hygas process.

Many other coal gasification projects to produce high BTU gas are under study. Since these processes are unlikely to become commercial by 1985, they are not reviewed here.

There is one low-BTU coal gasification project which has been announced recently and which merits a special comment. This is the Exxon 500 T/D coal gasification plant in Baytown, Texas. The announced principal justification for this plant is to produce low-BTU gas for heating use in the refinery. It is interesting to note that the Exxon refinery in Baytown will be the first oil refinery to obtain substantial fuel heating energy from coal. It also marks the beginning of the introduction of coal into the crude oil refining and petrochemical manufacturing processes.

Other low-BTU coal gasification plants which have been announced are planned exclusively for combined cycle electrical generating stations and are not intended to be used for gas manufacturing only.

A.3.7.1 - Hygas Coal Gasification Process

The Hygas gasification process has been in development since 1946. For the first time this year, the plant has operated continuously for more than one month and has successfully produced

SNG. The additional hydrogen needed in the methanation step had to come, however, from a steam reforming plant.

The gasifier in the Hygas process is a two stage fluidized bed reactor with a fluidized coal slurry drier. The first stage of the reactor operates at temperature from 1200 - 1400 F, while the second stage operates at 1600-1800 F. Pressure normally is 1000 psi.

In the gasifier, the hydrogen rich gases and steam move counter currently to coal through the two stages (entering at second stage), a gas solid disengaging section and then the coal slurry drier (Fig.A.3-6). The raw gases after purification enter a catalytic methanation reactor. The hydrogen entering the bottom second stage can be generated in several ways namely a steam-oxygen char gasifier, a steam-iron IGT gasifier using char or an electrothermal gasifier. Due to high costs of electrical power, the electrothermal method has been recently abandoned. A continuous steam-iron method is now in development stages, and will not likely reach large pilot plant testing until 1976. The steam-oxygen gasifier was to be integrated into the plant in the first quarter of 1974.

A.3.7.2 - CO_2-Acceptor Process for Coal Gasification

The CO_2-Acceptor process is a two fluidized-bed reactor process in which the exothermic reaction of magnesium oxide and calcium oxide with carbon dioxide provides the bulk of the heat needed to sustain the endothermic steam-coal gasification reactions. The calcium and magnesium carbonates (primarily $MgO \cdot CaCO_3$) are converted back to the oxides in a fluidized bed regenerator where fuel char is combusted with air at about 1870 F.

The devolatilization and gasification of coal (lignite) takes place in presence of steam at a temperature of about 1500 F (Fig.A.3-7).

A.3.7.3 - Synthane Process for Coal Gasification

In the Synthane gas process coal, steam and oxygen first enter a pretreater and then injected into a gasifier reactor. In the pre-

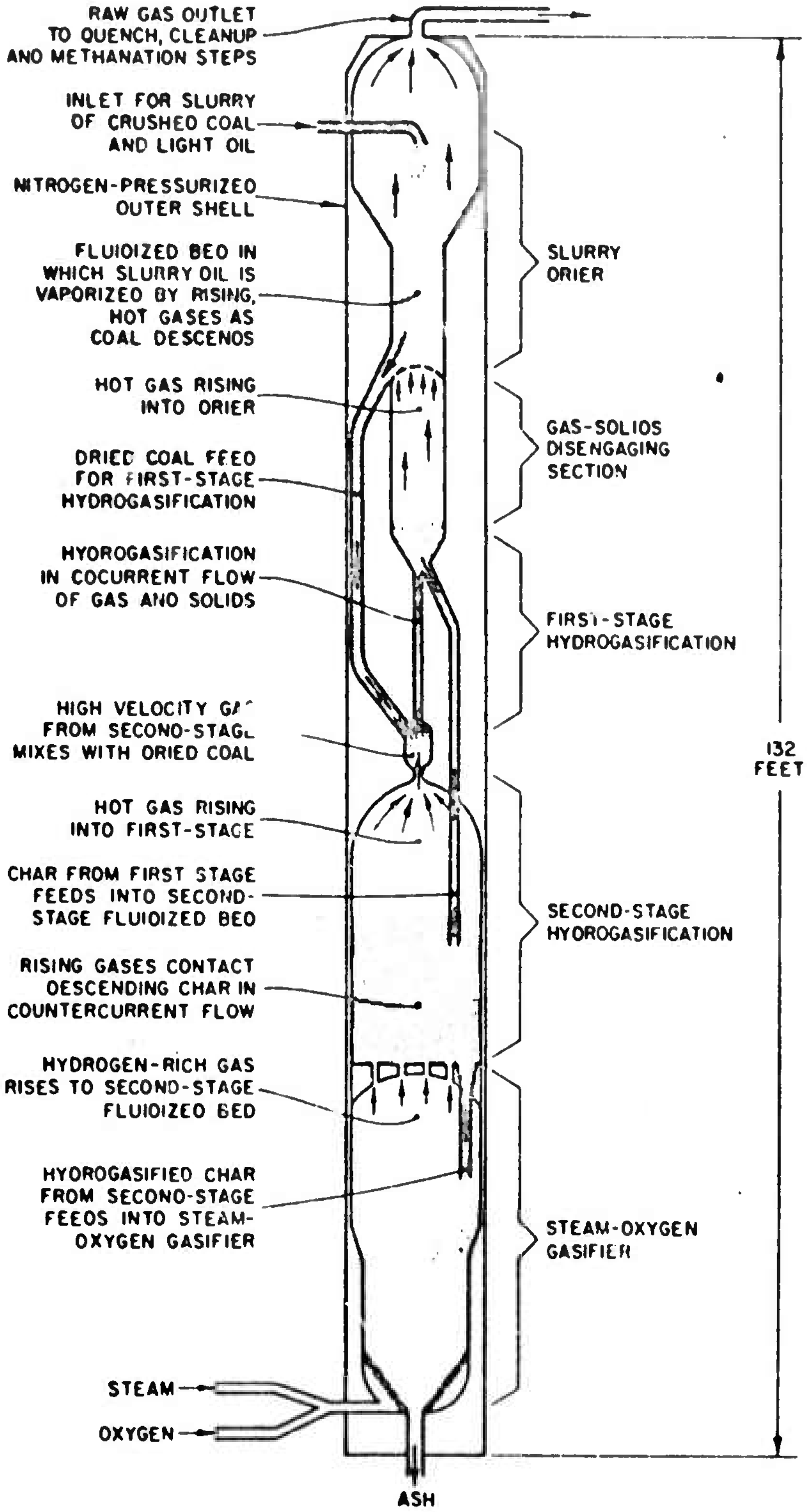

FIGURE A. 3-6: IGT HYGAS PILOT PLANT HYDROGASIFICATION REACTOR

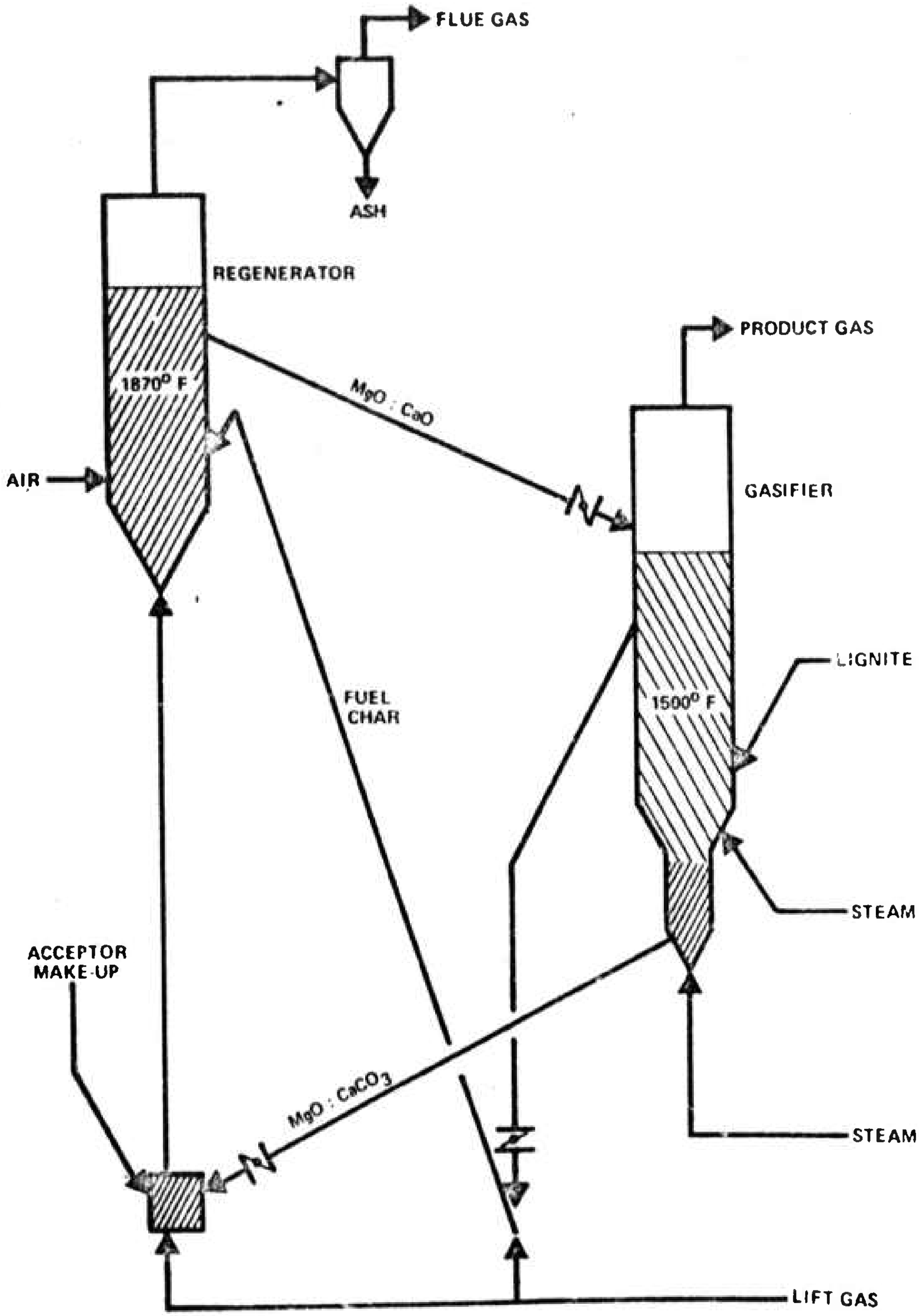

FIGURE A. 3-7: CO_2 ACCEPTOR PROCESS FLOW DIAGRAM

treater section, operating at about 750 F, partial devolatilization of coal occurs. The gasification reactions take place in a fluidized bed reactor. The reactor is operated at temperatures from 1850 F to 1100 F. The highest temperature is near the bottom of the reactor where oxygen and steam enter. Char residue is withdrawn at the bottom of the reactor (Fig. A.3-8).

The raw gas is first subjected to separation of particulates in a cyclone collector. The gas is then purified, reacted in a shift converter to adjust the CO and hydrogen ratio, and then converted to methane.

A.3.7.4 - Bigas Process for Coal Gasification

In the Bigas process steam and oxygen are injected near the bottom of the gasification reactor. The temperature at the bottom of the reactor is about 2800 F at which condition slagging of the ashes occurs. Slag is withdrawn at the bottom of the reactor (Fig.A.3-9). The carbon monoxide and hydrogen gases rise upward through the bed into which coal and addition steam are injected. This entrained flow section of the reactor operates between 1400 - 1700 F.

The raw product gases and unreacted char leave at the top of the reactor, where the char is separated in a cyclone and returned back to the lower section of the gasifier. The char free gases are cleaned, passed through a shift converter, further purified and then methanated in a catalytic reactor.

A.3.8 - Comparison of Various Processes of Coal Gasification

At the present time there are two commercial processes which are most widely used for coal gasification. They are the Lurgi and the Koppers-Totzek processes. The two processes, by far, dominate the coal to gas conversion field.

The Lurgi process, with all the inherent difficulties of a reactor with a mechanically actuated stirrer and ash removal equipment, is presently dominating the town gas and substitute natural gas generation field. In six years the total installed capacity of the Lurgi gasifiers will be in excess of 2000 MMCF/D with some 300 Lurgi gasifiers in the field.

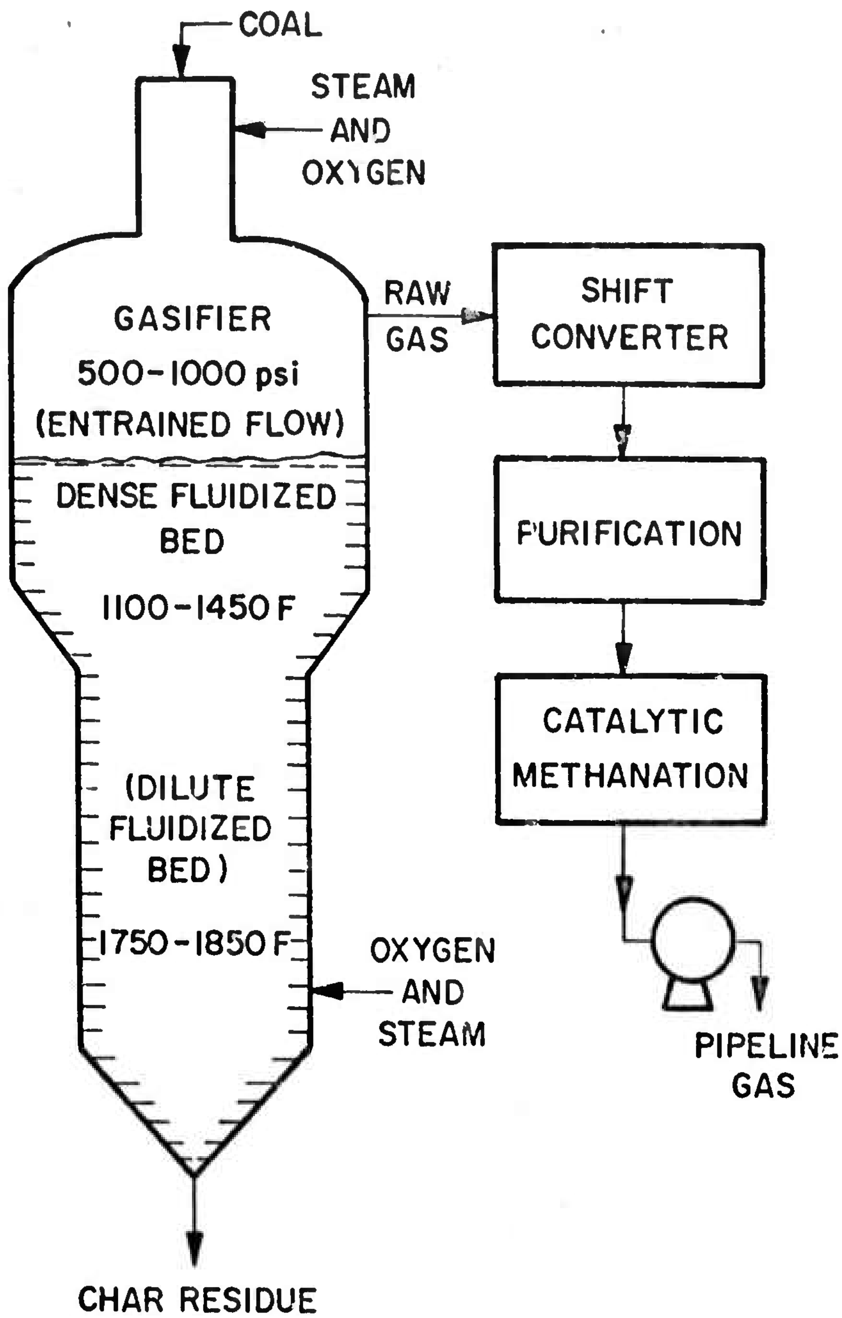

FIGURE A.3-8: SYNTHANE PROCESS FOR MAKING PIPELINE GAS FROM COAL

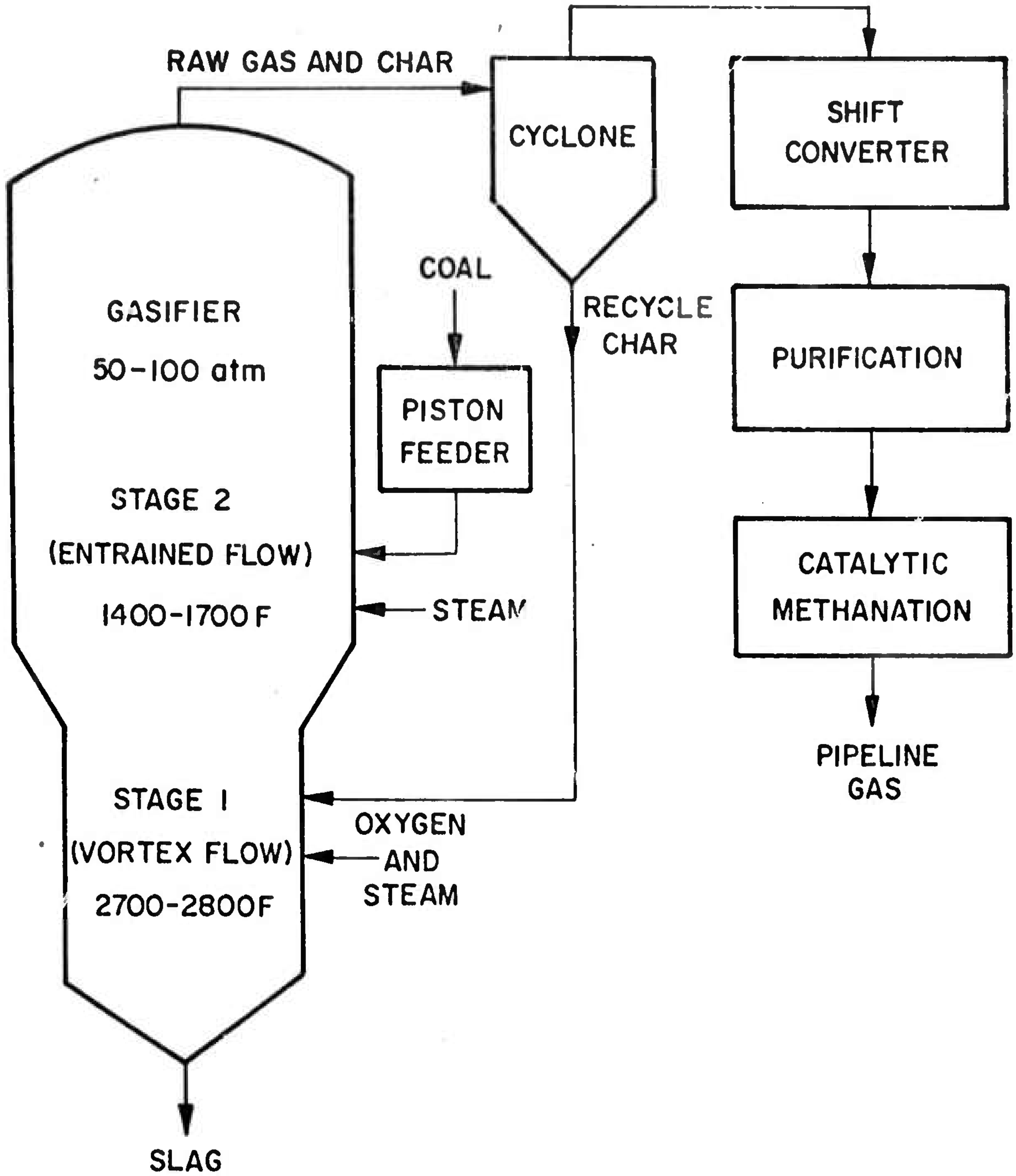

FIGURE A.3-9: BIGAS PROCESS FOR MAKING PIPELINE GAS FROM COAL

The technical reasons for the ability of the Lurgi Company to capture a large portion of the future coal to SNG gasification market are as follows:

1. The Lurgi process is the most tested process. Reactors have operated since 1936.
2. Methane and liquid hydrocarbons produced by the Lurgi gasifier constitute about 1/4 to 1/5 of the total energy content of the generated gas. These high BTU content products result in lower capital investment of SNG synthesis gas equipment.
3. The power requirements to produce SNG are lower than for the competing K-T process because the process is operated at a high pressure throughout.
4. Oxygen requirements are significantly lower (about 1/3 less) for the Lurgi process than for the K-T process.

The Koppers-Totzek process currently leads the Lurgi process in the total ammonia synthesis gas production from coal by at least a factor of two. The reasons for this are several. First, the K-T process generates essentially hydrogen and carbon monoxide free of tar, oils and phenols. Therefore, the production of hydrogen from coal is more direct and less clean-up of gases is required than in the processes where devolatilization of coal takes place. Second, the K-T process can accept a variety of coals or oil base feed stocks. Variations in coal properties do not strongly affect the method of operation of the reactor.

Third, the gasifier is simple in operation and does not have any moving metal parts subjected to hot coal gases.

The Winkler process does not currently enjoy wide use. There are 36 generators currently in operation (Ref. 15). The gasifier opates well with lignite or coal char which has been devolatilized. The ash fusion temperatures have to be high to prevent clinker agglomeration. The turn down ratio of the gasifier unit is rather limited and the plant has to operate within a narrow production range. The carbon gasification efficiency is not as high as for

the other two processes.

The Hygas process developed by IGT is the most advanced method of coal gasification in existence. It is still, however, at least five years from commercialization, unless a market for the char produced in the gasifier is found. Currently, there is a great deal of hope placed on the IGT fludized bed steam-iron method to resolve the problem of char utilization for hydrogen production. Since the pilot plant will not be operational for two more years, it is doubtful that a large coal gasification plant will be built to produce SNG using the Hygas process.

A similar char utilization and disposal problem has to be faced by the Synthane process which is much further from commercialization than the Hygas process. The CO_2 Acceptor process has encountered problems in the operation of the gasifier and the generator due to the presence of low melting point tacky liquids ($CaS-CaSO_4$) which collect fines. The pilot plant has not operated continuously for more than one hour. The primary advantage of the CO_2 Acceptor process in that it uses air rather than oxygen. The Bigas process will be tested in 1975 in a new pilot plant under construction.

A comprehensive comparison study of the Lurgi, Winkler and Koppers-Totzek gasification processes with the intent of deciding on the best ammonia synthesis gas generation process was reported in an Indian government report (Ref. 17).

A good description of the new coal gasification processes for SNG production at various stages of development is presented in Reference 11.

A.3.9 - Conclusions

There are now three commercially proven processes to convert coal, on a large scale, to a hydrogen and carbon monoxide rich gas. They are the Lurgi, Koppers-Totzek and the Winkler processes. The first two processes are almost exclusively used in all new large plants. (see Table A.3-2). The major exception is an air-blown, fluidized bed producer gas plant being built for Exxon (Carter Oil

TABLE A.3-2 - LIST OF COAL GASIFICATION PLANTS UNDER CONSTRUCTION

COMPANY	PLANT SITE	PROJECT	CAPACITY	ESTIMATED COST MM$	STATUS	LICENSOR	ENGINEERING	CONTRACTORS
El Paso Natural Gas	San Juan Co.,N.M.	Coal Gasification	288.0 MM CF/D	491.0	E 76	LURGI	STEARNS -R	-
Western Gasification	Burnham, N.M.	Coal Gasification	250.0 MM CF/D	380.0	E	LURGI	FLUOR	FLUOR
U.S. Bureau of Mines	Bruceton, Penna.	Coal Gasification	75.0 T/0	12.0	U 74	BUREAU MINES	RUST ENGG	RUST ENGG
Bituminious Coal Research	Monroeville	Coal Gasification	1.2 T/D	1.2	U 74	-	DRAVO	DRAVO
Bituminous Coal Research	Homer City,Pa.	Coal Gasification	120 T/D	-	U 75	-	-	STEARNS-R
Carter Oil Co.	Baytown, Texas	Coal Gasification	500 T/D	40.0	E 76	-	McKEE	McKEE
Panhandle Eastern	Campbell Co., Wyo.	Coal Gasification	250.0 MM CF/D	-	P	LURGI	-	-
Techno-Export CSR	Prague, Czechoslovakia	Coal Gasification	13.5 MM CF/D	-	U	UNITED	IBEG	IBEG
Techno-Export CSR	Prague, Czeck	Coal Gasification	68.D MM CF/D	-	U 74	TOPSOE	IBEG	IBEG
Hungarian Gas Trust	Pecs, Hungary	Coal Gasification	18.0 MM CF/D	-	C	CIFUINOUS	CIFUINOUS	CIFUINOUS

COMPANY	PLANT SITE	PROJECT	CAPACITY	ESTIMATED COST MM$	STATUS	LICENSOR	ENGINEERING	CONTRACTORS
Hungarian Gas Trust	Sopron, Hungary	Coal Gasification	1.8 MM CF/D	-	E	CIFUINDUS	CIFUINDUS	CIFUINDUS
Berlin Gaswerke	Berlin W.Germany	Coal Gasification	7.1 MM CF/D	-	C74	BASF/LURGI	LURGI	LURGI
Berlin Gaswerke	Berlin, W.Germany	Coal Gasification	38.9 MM CF/D	-	P75	-	-	-
Dortmunder Gaswerke	Dortmund W.Germany	Coal Gasification	27.0 MM CF/D	-	C74	BASF/LURGI	LURGI	LURGI
Stadtwerke Dortmund	Dortmund W.Germany	Coal Gasification	-	-	C	BASF/LURGI	LURGI	LURGI
Gen. Organization Gas+Elec.	Cairo, Egypt	Coal Gasification	1.0 MM CF/D	-	E	UNITED	IBEG	IBEG
General Egyptian Electric	Alexandria, Egypt	Coal Gasification	42.0 MM CF/D	-	E75	-	IBEG	IBEG
Osaka Gas Co.Ltd.	Osaka, Japan	Coal Gasification	34.0 MM CF/D	6.0	U74	ICI	DPG LTD/ MKK	MKK
Osaka Gas Co. Ltd.	Senboku, Japan	Coal Gasification	34.3 MM CF/D	-	E74	-	DPT LTD/ MKK	MKK
Saibu Gas Co. Ltd.	Fukuoka, Japan	Coal Gasification	11.4 MM CF/D	-	E74	BGC	DPT LTD/ MKK	DPG LTD/ MKK

COMPANY	PLANT SITE	PROJECT	CAPACITY	ESTIMATED COST MM$	STATUS	LICENSOR	ENGINEERING	CONTRACTORS
Saibu Gas Co. Ltd.	Saibu, Japan	Coal Gasification	5.7 MM CF/D	.3	U 74	ONIA GEGI	ISHII	MKK
Tokyo Gas Co. Ltd.	Omori, Japan	Coal Gasification	30.0 MM CF/D	-	E 74	HITACHI/ SELAS	HITACHI	HITACHI
Tokyo Gas Co. Ltd.	Toyoso, Japan	Coal Gasification	84.0 MM CF/D	-	E 74	-	HITACHI	HITACHI
Cogas Development Co.	Princeton, N.J.	Coal Refiner	2.5 T/D	-	C	-	-	BECHTEL
Old Ben Coal Corp.	Toledo, Ohio	Coal Refiner	900 T/D	75.0	P 78	-	-	-
Turkiye Komur Isletmeleri	Ankara, Turkey	Coal Refiner	120.0 MT/Y	12.5	E 75	OTTO	OTTO	OTTO
Co. Espanol Gas SA	Valencia Spain	Coal Gasification	1.8 MM CF/D	-	C	CIFUINDUS	CIFUINDUS	CIFUINDUS
Toho Gas Co. Ltd.	Sorami, Japan	Coal Gasification	56.0 MM CF/D	-	U 74	BGC	DPG LTD/MKK	MKK
Cities Service -Northern Natural Gas	Wyoming	Coal Gasification	250 MM CF/D	450	P 79	LURGI	-	-
American Natural Gas	North Dakota	Coal Gasification	250 MM CF/D	450	P 79	LURGI	-	-

Company) in Baytown, Texas.

The Lurgi process is used primarily for SNG synthesis gas and for town gas production. The Koppers-Totzek process is used primarily for ammonia synthesis gas production. While the first process produces a high-BTU gas, rich in methane, tars and light oil distillates,the second process has the advantage of generating a relatively pure mixture of carbon monoxide and hydrogen. Further treatment of raw gases and the water-gas shift conversion can produce essentially pure hydrogen gas.

On a smaller production scale, the blue water gas method is expected to be reintroduced for the manufacture of hydrogen rich gases.

The fluidized bed processes for SNG production, which are currently being developed in the United States, are not ready yet for commercialization. Except for the IGT Hygas process, none of the projects which are currently at pilot plant stage of development are expected to be ready for commercialization in the near future.

In the low-BTU gas production (roughly 50% N_2, remainder H_2, CO and CO_2), fluidized bed gasification is expected to be the major new method of producing gas on a large scale. On a smaller scale, gas producers are expected to be reintroduced to American industry.

Despite the current high cost of natural gas, naphtha and distillate fuels, some 35 hydrogen manufacturing plants currently planned or under construction will use these fuels as feed stocks (Table A.3-1). Only one plant will probably use coal.

With all the announced planned activity in coal gasification for SNG production, the major source of SNG until 1980 will be the completed liquid hydrocarbon cracking plants (562 MMCF/D) capacity (Ref. 18) and plants currently under construction (705 MMCF/D additional capacity by 1975 - Table A.3-3).

It appears that despite the relative abundant supply of coal,

TABLE A.3-3 - LIST OF SUBSTITUTE NATURAL GAS PLANTS UNDER CONSTRUCTION

COMPANY	PLANT SITE	PROJECT	CAPACITY	ESTIMATED COST MM$	STATUS	LICENSOR	ENGINEERING	CONTRACTORS
Tuscon Gas&Elec. Co.	Tuscon, Arizona	Substitute Natural Gas	100.0 MM CF/D	30.0	E 75	LURGI	FLUOR	FLUOR
Florida Gas Co.	Jackson-ville, Fla.	Substitute Natural Gas	-	-	P	-	-	-
Gasco Inc.	Honolulu, Hawaii	Substitute Natural Gas	16.0 MM CF/D	-	U 74	LURGI	PARSONS RM	PARSONS RM
Central Illinois Light Co.	Peoria, Illinois	Substitute Natural Gas	60.0 MM CF/D	16.0	P	-	-	-
Northern Illinois Gas Co.	Morris, Illinois	Substitute Natural Gas	184.0 MM CF/D	-	U 74	BGC	BECHTEL/ WOODALL-D	BECHTEL
Peoples Gas Light	Will County, Illinois	Substitute Natural Gas	160 MM CF/D	80.0	U 74	BGC/KELLOGG	KELLOGG	KELLOGG
APCO Oil Corp.	Baltimore, Maryland	Substitute Natural Gas	125 MM CF/D	-	P 74	-	-	-
Baltimore Gas & Elec.	Baltimore, Md.	Substitute Natural Gas	60.0 MM CF/D	25.0	P	BASF/LURGI	S& W Kellogg	S & W

COMPANY	PLANT SITE	PROJECT	CAPACITY	ESTIMATED COST MM$	STATUS	LICENSOR	ENGINEERING	CONTRACTORS
Boston Gas Co.	Everett, Mass	Substitute Natural Gas	40.0 MM CF/D	-	C	JSG/UOP	BADGER	BADGER
Consumers Power Co.	Marys-ville, Michigan	Substitute Natural Gas	220.0 MM CF/D	150.0	U	BGC	H & G	LUMMUS
Cities Service S-G-Inc.	Diamond, Missouri	Substitute Natural Gas	125.0 MM CF/D	-	E 75	BASF/LURGI	S & W	S & W
Public Service Elec.& Gas	Linden, N.J.	Substitute Natural Gas	125.0 MM CF/D	-	U 74	BGC	FW	FW
South Jersey Energy Co.	Glouster Co., N.J.	Substitute Natural Gas	125.0 MM CF/D	30.0	E 74	BGC	LUMMUS	LUMMUS
Brooklyn Union Gas	Brooklyn, N.Y.	Substitute Natural Gas	60.0 MM CF/D	24.0	C	BGC	H & G	LUMMUS
Northwest Natural Gas Co.	Portland, Oregon	Substitute Natural Gas	100.0 MM CF.D	25.0	E	LURGI	FLUOR	FLUOR
Transco Energy Co.	Delaware Co.,Penn.	Substitute Natural Gas	250.0 MM CF/D	85.0	E	BASF/LURGI	FLUOR	-
Coastal States Energy	Corpus Christi, Texas	Substitute Natural Gas	200 MM CF/D	33.0	P 74	BGC	PRITCHARD	PRITCHARD

the activity to produce hydrogen rich gases seems to be in the steam reforming of petroleum liquids. The exceptions are the SNG coal gasification plants. The profit on the operation of these plants is guaranteed by the Federal Power Commission. The reason for the lack of investment commitment outside of the utility industry is probably due to the uncertainty surrounding future petroleum cost and availability, as well as the cost and availability of investment capital required for these large plants.

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A.4 - THERMOCHEMICAL HYDROGEN PRODUCTION

A.4.1 - Introduction

A promising method for the production of hydrogen under consideration is a cyclic thermochemical process in which the energy to separate hydrogen from water is in the form of heat.

One method in commercial practice today to separate hydrogen from water is electrolysis. However, electrolysis of water is faced with inherent thermodynamic limitations on the efficiency of initial conversation of thermal to electrical energy. Current conversion efficiencies are in the range 30-40%; while future projections indicate 50% as an achieveable goal. This, in addition to an expected maximum realizable electrolytic efficiency of around 85-95% limits the overall efficiency of electrolysis for hydrogen production expected in the future to about 35-50%. This limitation has prompted attempts to find alternate means of producing hydrogen from water by processes that exceed these efficiencies.

The decomposition of water may be accomplished in a single, direct chemical reaction. However, this requires extremely high temperatures, greater than 2000°C. Heat sources capable of supplying this temperature are not readily available and thus it appears to be an impractical process for hydrogen production.

Theoretically, however, by employing a process whereby in a series of two or more chemical reactions water reacts with an intermediate to form products that may be thermally decomposed to produce hydrogen and oxygen in separate reaction stages and regenerate the original intermediate compound, hydrogen may be produced from water at much lower temperatures. In this scheme, the thermal energy in nuclear fission reactors and nuclear fusion reactors, and solar and geothermal energy can be made <u>directly</u> available to the separation process. Then with the appropriate selection of a reaction scheme and the proper operating temperatures, this approach may be capable of yielding a higher overall efficiency of conversion of thermal energy and water to hydrogen than the electrical process.

Most of the effort in this area has focused on the thermochemical production of hydrogen employing a nuclear heat source. Thus most of the proposed reaction schemes have been strongly coupled to actual or anticipated reactor core coolant exit temperatures. Table A.4-1 indicates these temperatures.

While thermochemical processes to produce hydrogen are not in operation today, there is extensive research and development work in this area going on around the world. The largest such effort by far is at the Euratom Laboratory at Ispra, Italy, with a project begun in 1969 and presently employing over 50 people. Other presently active projects include German efforts at Julich (KFA) and the University of Aachen, and U.S. efforts at Institute of Gas Technology Argonne National Laboratory, Los Alamos National Laboratory, General Electric Company, and General Atomic Company. The current status of these efforts and their ultimate potential will be discussed below.

A.4.2 - Physical Principles & Theory

Funk and Reinstrom (Refs. 1,2) analyzed the problem of the energy requirements for producing H_2 from water. For any reversible process operated at constant temperature and pressure, the work (W) and heat (Q) requirements to decompose each gram-mole of H_2O are:

$$W = \Delta G$$
$$Q = T\Delta S$$

where ΔG and ΔS are the Gibbs free energy change and the entropy change per gram-mole of water. Thus for the reaction

$$H_2O(\ell) \rightarrow H_2(g) + \tfrac{1}{2}\, O_2(g)$$

at 25°C and 1 atm. these requirements become (Ref. 3)

$$W = \Delta G = 56.69 \text{ Kcal/g-mole}$$
$$Q = T\Delta S = 11.63 \text{ Kcal/g-mole}$$

TABLE A.4-1: NUCLEAR REACTOR COOLANT TEMPERATURE

Reactor Type	Coolant	Reactor Core Coolant Exit Temp., °C
Boiling-water reactor (BWR)	H_2O	250 - 325
Pressurized-water reactor (PWR)	H_2O	275 - 350
Low-temperature gas-cooled reactor (LTGR)	CO_2	350 - 575
Boiling-water reactor with superheat (BWR/SH)	H_2O	450 - 575
Liquid-metal fast-breeder reactor (LMFBR)	LNa	450 - 625
High-temperature gas-cooled reactor (HTGR)	He	780 - 900
High-temperature gas-cooled reactor (Germany-pebble bed core)	He	900 - 1000

and the enthalpy change (ΔH) for the reaction becomes

$$\Delta H = \Delta G + T\Delta S = 68.32 \text{ Kcal/mole}$$

Thus, in the case of electrolysis at room temperature, most of the energy (83.7%) to produce H_2 must come from electric power (i.e., useful work), the other 16.3% being supplied as heat. Electric power requirements can only be reduced by electrolyzing at elevated temperature, thereby increasing T S and lowering G.

Funk and Reinstrom's analysis indicated that, in theory, it should be possible to develop multistep processes for which the power requirements are essentially reduced to zero at a technically feasible temperature (1100°C). Ideally, there would be some element or compound M, which would react in a two-step process according to one or the other of the following general schemes:

<u>Oxide Reactions</u>:

$$M + H_2O \rightarrow MO + H_2 \quad (\text{"Low" temperature})$$
$$MO \rightarrow M + \tfrac{1}{2}O_2 \quad (\text{"High" temperature})$$

<u>Hydride Reactions</u>:

$$M + H_2O \rightarrow MH_2 + \tfrac{1}{2}O_2 \quad (\text{"Low" temperature})$$
$$MH_2 \rightarrow M + H_2 \quad (\text{"High" temperature})$$

Requiring that the two-step process be feasible at temperatures no higher than 1100°C, Funk and Reinstrom made a systematic search of the elements and their monoxides and hydrides. They concluded: "No compounds which could yield an efficient two-step process were found. Furthermore, based on semi-empirical correlations, it appears unlikely that a compound exists, or can be synthesized, which will yield a two-step chemical process superior to water electrolysis". In fact they questioned the existence of any process which would have a higher overall efficiency than water electrolysis. (Overall efficiency (η) as defined here is

$$\eta = \frac{\Delta H_f}{Q}$$

where ΔH_f is the heat of formation (or combustion) of a mole of water from hydrogen and oxygen and Q is the total heat required by the

overall process to split a mole of water into hydrogen and oxygen. Since water may exist in either the gaseous or liquid state, the heat of combustion of hydrogen depends on the final product state. Consequently, the lower heating value (LHV) for hydrogen corresponds to water vapor products, while the higher heating value (HHV) is for liquid water and hence includes the heat of condensation. Most efficiencies are calculated on the basis of the LHV. The total heat required by the overall process, Q, includes the heat necessary for the individual endothermic reactions as well as extra heat needed to supply pumping power, work of separation, miscellaneous losses, etc.)

Thus most of the attention has been focused on the development of processes employing three or more steps. In principle, thousands of combinations of multi-component closed-cycle chemical systems exist that might yield a workable thermochemical water-splitting process. In order to effectively select the most promising cycles, it is necessary to develop a series of criteria to screen potential candidate processes. Ideally, these criteria should include the process overall efficiency based on both thermodynamic and kinetic factors, the required maximum temperature of the process and its compatibility with various nuclear reactor or other heat sources, materials compatibility, and ecological and safety constraints. Unfortunately, efforts to date have primarily been directed towards establishing thermodynamic feasibility of cycles comparatible with various nuclear reactor heat sources.

Nevertheless, thermochemical processes for hydrogen production are promising because, although thermochemical cycles are also Carnot efficiency limited, the ideal overall efficiency of a thermochemical cycle is higher than the equivalent Carnot efficiency of a heat-engine cycle operating between the same temperatures. Also, it may be possible to employ higher temperatures than can be used in a steam-electric generating plant, thus providing more effective use of the thermal energy available from the primary heat source.

A.4.3 - Current Status of Technology

Hydrogen production by thermochemical processes has been the subject of increasing interest the past 5 years. Over forty schemes have been proposed in the literature and there are strong indications that additional, very promising, processes have been developed that will not be published until patents have been received. Currently major studies are underway to find new processes and develop existing schemes at the Euratom facilities in Ispra, Italy; the Nuclear Research Center of Juelich West Germany; Los Alamos Laboratory; Lawrence Livermore Laboratory; the Institute of Gas Technology; General Atomic; and General Electric Research Laboratories.

In order to develop a perspective of the scope of the various processes reported to date, 22 schemes are shown in Tables A.4-2 to A.4-4. These schemes are discussed in greater detail below. However, it should be noted that these processes are in the early stages of development. As yet, none of these cycles have been proven experimentally, even at the bench scale. Thus extrapolation from the existing data base to estimate process plant cost and overall efficiency is hazardous.

A.4.3.1 - Halide Processes

Many of the proposed processes for the thermochemical production of hydrogen are based on the chemistry of halide compounds. Nine of these schemes are shown in Table A.4-2. The majority of this work is underway at the Euratom facilities in Ispra, Italy (Refs. 4,5).

The process that has received the most attention is the Mark 1 cycle. This cycle uses compounds of mercury, bromine and calcium. Considerable effort has been devoted towards equilibrium and kinetics measurements of reaction 1 - the hydrolysis of calcium bromide at various temperatures. The chemistry of the reactions of mercurous bromide with hydrobromic acid and the reaction of mercury bromide with calcium hydroxide are also under investigation. The only data previously available in the literature was on the dissociation of mercuric oxide. The Mark 1 cycle has been subjected to a block diagram analysis which resulted in a predicted overall efficiency of 49.3% (LHV).

TABLE A.4-2: HALIDE PROCESSES

1. Mark 1 (Euratom)

$CaBr_2 + 2H_2O \rightarrow Ca(OH)_2 + 2HBr$	$730^{\circ}C$
$2HBr + Hg \rightarrow HgBr_2 + H_2$	$250^{\circ}C$
$HgBr_2 + Ca(OH)_2 \rightarrow CaBr_2 + HgO + H_2O$	$200^{\circ}C$
$HgO \rightarrow Hg + \frac{1}{2}O_2$	$600^{\circ}C$

2. Mark 1B (Euratom)

$CaBr_2 + 2H_2O \rightarrow Ca(OH)_2 + 2HBr$	$730^{\circ}C$
$2HBr + Hg_2Br \rightarrow 2HgBr_2 + H_2$	$120^{\circ}C$
$HgBr_2 + Hg \rightarrow Hg_2Br_2$	$120^{\circ}C$
$HgBr_2 + Ca(OH)_2 \rightarrow CaBr_2 + HgO + H_2O$	$200^{\circ}C$
$HgO \rightarrow Hg + \frac{1}{2}O_2$	$600^{\circ}C$

3. Mark 1C (Euratom)

$2\ CaBr_2 \quad 4\ H_2O \rightarrow 2\ Ca(OH)_2 + 4\ HBr$	$730^{\circ}C$
$4HBr + Cu_2O \rightarrow 2\ CuBr_2 \quad H_2O + H_2$	$100^{\circ}C$
$2\ CuBr_2 + 2\ Ca(OH)_2 \rightarrow 2\ CuO + 2\ CaBr_2 + 2H_2O$	$100^{\circ}C$
$2\ CuO \rightarrow Cu_2O + \frac{1}{2}O_2$	$900^{\circ}C$

4. Mark 1S (Euratom)

$SrBr_2 + H_2O \rightarrow SrO + 2\ HBr$	$800^{\circ}C$
$2HBr + Hg \rightarrow HgBr_2 + H_2$	$200^{\circ}C$
$SrO + HgBr_2 \rightarrow SrBr_2 + Hg + \frac{1}{2}O_2$	$500^{\circ}C$

5. Mark 5 (Euratom)

$CaBr_2 + H_2O + CO_2 \rightarrow CaCO_3 + 2HBr$	$600^{\circ}C$
$CaCO_3 \rightarrow CaO + CO_2$	$900^{\circ}C$
$2HBr + Hg \rightarrow HgBr_2 + H_2$	$200^{\circ}C$
$HgBr_2 + CaO + nH_2O \rightarrow CaBr_2\ (aq) + HgO$	$200^{\circ}C$
$HgO \rightarrow Hg + \frac{1}{2}O_2$	$600^{c}C$

6. Mark 7 (Eruatom)

$6\ FeCl_2 + 8\ H_2O \rightarrow 2\ Fe_3O_4 + 12\ HCl + 2H_2$	650°C
$2\ Fe_3O_4 + \frac{1}{2}O_2 \rightarrow 3\ Fe_2O_3$	350°C
$3\ Fe_2O_3 + 18\ HCl \rightarrow 6\ FeCl_3 + 9\ H_2O$	120°C
$6\ FeCl_3 \rightarrow 6\ FeCl_2 + 3Cl_2$	420°C
$3\ H_2O + 3Cl_2 \rightarrow 6\ HCl + 3/2O_2$	800°C

7. Mark 8 (Euratom)

$6\ MnCl_2 + 8\ H_2O \rightarrow 2\ Mn_3O_4 + 12\ HCl + 2H_2$	700°C
$3\ Mn_3O_4 + 12\ HCl \rightarrow 6\ MnCl_2 + 3MnO_2 + 6\ H_2O$	100°C
$3\ MnO_2 \rightarrow Mn_3O_4 + O_2$	900°C

8. Mark 9 (Euratom)

$6\ FeCl_2 + 8\ H_2O \rightarrow 2\ Fe_3O_4 + 12\ HCl + 2H_2$	650°C
$2\ Fe_3O_4 + 3Cl_2 + 12\ HCl \rightarrow 6\ FeCl_3 + 6\ H_2O + O_2$	150-200°C
$6\ FeCl_3 \rightarrow 6\ FeCl_2 + 3Cl_2$	420°C

9. Agnes (G.E.)

$3FeCl_2 + 4H_2O \rightarrow Fe_3O_4 + 6HCl + H_2$	450-750°C
$Fe_3O_4 + 8HCl \rightarrow FeCl_2 + 2FeCl_3 + 4H_2O$	100-110°C
$2FeCl_3 \rightarrow 2FeCl_2 + Cl_2$	300°C
$Cl_2 + Mg(OH)_2 \rightarrow MgCl_2 + \frac{1}{2}O_2 + H_2O$	50 -90°C
$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl$	350°C

The Mark 1 process has some particularly attractive characteristics. Since the maximum temperature required is 730°C the primary nuclear reactor coolant need only be 800-850°C - a temperature well in the range of actual HTGR's. Also all reaction products are easily separated and all by-products formed can be reinjected at other points in the cycle. However, the Mark 1 cycle is not without drawbacks. The use of mercury entails a high inventory cost and presents the possibility of pollution in case of leakage. The use of highly corrosive hydrobromic acid presents problems for construction materials.

The above mentioned drawbacks prompted the definition of alternative schemes which modify the Mark 1 cycle. The Mark 1B differs from the Mark 1 by the reaction between mercury and hydrobromic acid. Realizing this reaction in two steps, as indicated in Table A.4-2, it is possible to decrease the reaction temperature from 200°C to 120°C. This permits a better internal heat recuperation, a higher rate for the reaction, and consequently a lower mercury inventory. Studies are underway on the equilibrium and kinetics of these two reactions. In an attempt to avoid the use of mercury, the Mark 1 was modified (Mark 1C) to employ copper instead of mercury. The drawbacks of the Mark 1C cycle are in the higher temperature (900°C) necessary to dissociate the copper oxide and in the halved production of hydrogen for the same amount of circulating products as in the mercury cycles. Also a key to the cycle is the second reaction about which little is known. Work is in progress on this reaction at Euratom.

Another variation of the Mark 1 cycle, the Mark 1S, employs strontium instead of calcium. Besides reducing the cycle to three steps, at the expense of a slightly higher temperature, the major advantage of employing strontium bromide is the possibility, calculated from thermodynamic data, of carrying out the third reaction in the solid-phase. This avoids the manipulation of the concentrated solutions of bromides and results in a lower hydrobromic acid concentration. While this process has been patented, the third reaction has as yet not been tested in the laboratory. Obviously, the second reaction in the Mark 1S cycle may be replaced by the second and third reactions in the Mark 1B cycle.

The Mark 5 cycle employs compounds of carbon, as well as mercury, bromine and calcium. The difference from the Mark 1 is the lower temperature for the hydrolysis reaction. From preliminary tests, for the same hydrobromic acid concentration, a 200°C lowering of temperature in the hydrolysis reaction can be obtained. This lower temperature could help in solving the problem of construction material in the chemical reactor. However, this advantage has to be paid by the higher temperature needed for the dissociation of calcium carbonate. Tests on the first reaction are in progress. This cycle can also be modified by the introduction of copper instead of mercury (as in Mark 1C) or by performing the reaction between mercury and hydrobromic acid in two steps (as in Mark 1B).

In the study of new cycles to produce hydrogen by decomposing water through a series of chemical reactions, processes based on iron chlorides and manganese chlorides have been proposed. The main characteristics of this family is to use as intermediate compounds, only combinations of iron (manganese), chlorine, oxygen and hydrogen. The Mark 7 cycle is one of the iron-chlorine family; the basic reaction is the hydrolysis of ferrous chloride at high temperature to produce hydrogen. Experimental studies are in progress on this scheme. Two modifications of the Mark 7 have been proposed - Mark 7A and Mark 7B. In the Mark 7A cycle the first three reactions are identical with Mark 7, but some of the Fe_2O_3 is chlorinated by chlorine to produce oxygen. This reaction is used in place of reaction five of Mark 7. In the Mark 7B, the first 2 reactions are the same as in Mark 7, but then all the ferric oxide is chlorinated by chlorine, to form anhydrous ferric chloride and oxygen; this chloride is thermally decomposed and HCl obtained from reaction 1 reacts with some of the oxygen to produce the chlorine necessary for the chlorination of Fe_2O_3.

The Mark 8 cycle is based on the hydrolysis of manganese chloride. The first reaction has been described in the literature where there is some disagreement about the composition of the manganese oxide obtained. A similar reaction to reaction two, employing sulfuric acid instead of hydrochloric acid, is also described in the literature. The third reaction, while requiring a high temperature, doesn't seem to pose any practical difficulty. Work is planned on

reactions one and two.

The Mark 9 cycle also belongs to the iron-chlorine family, however, it is defined by only 3 reactions. It is built on the hydrolysis of ferrous chloride. In reaction 2 magnetite is simultaneously oxidized and chlorinated by a mixture of hydrogen chloride and chlorine with formation of ferric chloride and evolution of oxygen. Experimental work on this reaction has been started.

The final halide process listed in Table A.4-2 is the Agnes Process (Ref. 6) proposed by Wentorf and Hanneman at General Electric. In this process iron, chlorine, and magnesium are cycled through five reactions. This process can operate at relatively low temperatures if necessary, which limits the overall efficiency compared to processes where heat is available at higher temperatures. On the other hand, at lower temperatures cheaper heat, such as sunshine or partially degraded nuclear heat rejected from another coupled process, can be used and corrosion problems are less severe. This process has been subjected to thermochemical analysis only, and the authors report an overall efficiency of 41% (LHV).

A.4.3.2 - Reverse Deacon Processes

A series of processes have been developed around the reaction of chlorine gas and water to form hydrochloric acid and oxygen (Table A.4-3). The reverse reaction, the oxidation of hydrochloric acid, has been of commercial interest for almost a hundred years and is known as the Deacon process for chlorine manufacture. By increasing the temperature the equilibrium in the Deacon reaction can be reversed to produce hydrogen chloride and oxygen.

The first cycle uses vanadium chlorides in a four step cycle and was first proposed by Funk and Reinstrom in 1964. Funk calculated an overall efficiency of 18% (HHV) for the process. This figure is lower than most reported efficiencies for other processes, since Funk included the work of separation in his calculations. Other chlorides of the Group V family such as tantalum were considered and found less promising than vanadium (Ref. 1).

TABLE A.4-3: REVERSE DEACON PROCESSES

1. Vanadium Chloride Process (Allison Div., G.M.)

$H_2O + C\ell_2 \rightarrow 2\ HC\ell + \frac{1}{2}O_2$	$800^\circ C$
$2VC\ell_2 + 2HC\ell \rightarrow 2VC\ell_3 + H_2$	$25^\circ C$
$4\ VC\ell_3 \rightarrow 2VC\ell_4 + 2\ VC\ell_2$	$700^\circ C$
$2\ VC\ell_4 \rightarrow 2VC\ell_3 + C\ell_2$	$25^\circ C$

2. Mark 3 (Euratom)

$H_2O + C\ell_2 \rightarrow 2HC\ell + \frac{1}{2}O_2$	$800^\circ C$
$2\ VOC\ell + 2\ HC\ell \rightarrow 2\ VOC\ell_2 + H_2$	$170^\circ C$
$4\ VOC\ell_2 \rightarrow 2\ VOC\ell + 2\ VOC\ell_3$	$600^\circ C$
$2\ VOC\ell_3 \rightarrow 2\ VOC\ell_2 + C\ell_2$	$200^\circ C$

3. Mark 4 (Euratom)

$H_2O + C\ell_2 \rightarrow 2HC\ell + \frac{1}{2}O_2$	$800^\circ C$
$2HC\ell + S + 2\ FeC\ell_2 \rightarrow H_2S + 2\ FeC\ell_3$	$100^\circ C$
$H_2S \rightarrow H_2 + \frac{1}{2}S_2$	$800^\circ C$
$2\ FeC\ell_3 \rightarrow 2\ FeC\ell_2 + C\ell_2$	$420^\circ C$

4. Mark 6 (Euratom)

$C\ell_2 + H_2O \rightarrow 2HC\ell + \frac{1}{2}O_2$	$800^\circ C$
$2HC\ell + 2CrC\ell_2 \rightarrow 2CrC\ell_3 + H_2$	$170^\circ C$
$2CrC\ell_3 + 2\ FeC\ell_2 \rightarrow 2\ CrC\ell_2 + 2FeC\ell_3$	$700^\circ C$
$2FeC\ell_3 \rightarrow 2FeC\ell_2 + C\ell_2$	$350^\circ C$

The Mark 3 cycle proposed by De Beni is similar to the cycle of Funk and Reinstrom, however, the oxichlorides of vanadium are substituted for the vanadium chlorides. This substitution is suggested by the lower affinities of the oxichlorides towards water.

The Mark 4 cycle, patented by Hardy, involves the iron chlorides and sulfur. The hydrochloric acid, formed in the reverse Deacon process, reacts with sulfur and ferrous chloride with oxidation of ferrous chloride to ferric chloride with the evolution of hydrogen sulphide. The ferric chloride and hydrogen sulphide are then separately thermally decomposed. There seems to be no current work underway on this process.

The Mark 6 cycle is based only on thermodynamic calculations. At the temperatures envisaged for the second reaction the two chromium chlorides are solids and therefore, it is proposed to carry out the reaction in a bath of molten salts. Also, in the third reaction, iron chloride $FeCl_2$ could be substituted for by vanadium chloride VCl_2. The Mark 6C, a modification of the Mark 6 cycle, employs a copper chloride reaction in a 5 step scheme to overcome the eventual difficulty of the direct decomposition of the iron trichloride. All the reactions appear quite feasible from the available thermodynamic data, however, no experimental work has been performed to date.

A.4.3.3 - Metal Processes

A carbon-iron oxide process has been suggested by De Beni and Marchetti (Ref. 7). It is a simple reaction sequence, employing a three step cycle. This process, although thermodynamically feasible, requires a rather high temperature (1425°C). Since this temperature is beyond the range of current nuclear energy heat sources, work at Euratom on this process has stopped.

Another carbon-iron process was proposed by C.G. Von Fredersdorff of the Institute of Gas Technology in 1959 (Ref. 8). The heart of the scheme is the production of H_2 by the steam-iron process, a process of proven feasibility. However, the proposed process calls for the decomposition of CO_2 under conditions that are highly unfavorable thermodynamically. It is proposed to decompose the CO_2 to CO in a chemonuclear reactor at 315°C and the major obstacle to the

TABLE A.4-4: METAL PROCESSES

1. Carbon-Iron Process (Euratom)

$C + H_2O \rightarrow CO + H_2$	$700^\circ C$
$CO + 2\ Fe_3O_4 \rightarrow C + 3Fe_2O_3$	$250^\circ C$
$3Fe_2O_3 \rightarrow 2Fe_3O_4 + \frac{1}{2}O_2$	$1425^\circ C$

2. Carbon Dioxide-Iron Process (IGT)

$Fe + H_2O \rightarrow FeO + H_2$	
$3FeO + H_2O \rightarrow Fe_3O_4 + H_2$	550-
$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$	$950^\circ C$
$FeO + CO \rightarrow Fe + CO_2$	
$2CO_2 \rightarrow 2CO + O_2$	$315^\circ C$

3. Sulfur Dioxide-Iron Process (IGT)

$Fe_3O_4 + 2H_2O + 3\ SO_2 \rightarrow 3\ FeSO_4 + 2\ H_2$	$125^\circ C$
$3FeSO_4 \rightarrow 3/2\ Fe_2O_3 + 3/2\ SO_2 + 3/2\ SO_3$	$725^\circ C$
$3/2\ Fe_2O_3 + \frac{1}{2}\ SO_2 \rightarrow Fe_3O_4 + \frac{1}{2}\ SO_3$	$925^\circ C$
$2\ SO_3 \rightarrow 2\ SO_2 + O_2$	$925^\circ C$

4. Cesium Process (Aerojet)

$2Cs + 2H_2O \rightarrow 2CsOH + H_2$	$100^\circ C$
$2CsOH + 3/2O_2 \rightarrow H_2O + 2CsO_2$	$500^\circ C$
$2CsO_2 \rightarrow Cs_2O + 3/2\ O_2$	$700^\circ C$
$Cs_2O \rightarrow 2Cs + \frac{1}{2}O_2$	$1200^\circ C$

5. Catherine Process (G.E.)

$3I_2 + 6\ LiOH \rightarrow 5\ LiI + LiIO_3 + 3H_2O$	$100\text{-}190^\circ C$
$LiIO_3 + KI \rightarrow KIO_3 + LiI$	$0^\circ C$
$KIO_3 \rightarrow KI + 1.5O_2$	$650^\circ C$
$6LiI + 6H_2O \rightarrow 6HI + 6LiOH$	$450\text{-}600^\circ C$
$6HI + 3\ Ni \rightarrow 3NiI_2 + 3H_2$	$150^\circ C$
$3NiI_2 \rightarrow 3Ni + 3I_2$	$700^\circ C$

6. Lithium Nitrate Process (Argonne Nat. Labs)

$LiNO_2 + I_2 + H_2O \rightarrow LiNO_3 + 2HI$	25°C
$2\ HI \rightarrow H_2 + I_2$	425°C
$LiNO_3 \rightarrow LiNO_2 + \frac{1}{2}O_2$	425°C

7. Tin Oxide Process (Gaz de France)

$Sn + 2H_2O \rightarrow 2H_2 + SnO_2$	400°C
$2\ SnO_2 \rightarrow 2\ SnO + O_2$	1700°C
$2\ SnO \rightarrow SnO_2 + Sn$	700°C

8. Beulah Process (G.E.)

$2\ Cu + 2HC\ell \rightarrow H_2 + 2\ CuC\ell$	100°C
$4\ CuC\ell \rightarrow 2\ CuC\ell_2 + 2\ Cu$	30-100°C
$2\ CuC\ell_2 \rightarrow 2\ CuC\ell + C\ell_2$	500-600°C
$C\ell_2 + Mg(OH)_2 \rightarrow MgC\ell_2 + H_2O + \frac{1}{2}O_2$	80°C
$MgC\ell_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HC\ell$	350°C

9. Mark 2 (Euratom)

$Mn_2O_3 + 4\ NaOH \rightarrow 2\ Na_2O \cdot MnO_2 + H_2O + H_2$	800°C
$2\ Na_2O \cdot MnO_2 + nH_2O \rightarrow 4\ NaOH(aq) + 2\ MnO_2$	100°C
$2\ MnO_2 \rightarrow Mn_2O_3 + \frac{1}{2}O_2$	600°C

development of this process will be the development of the chemonuclear reactor itself.

Another process developed at the Institute of Gas Technology involving iron oxides and iron sulfides employs sulfur dioxide in a four step scheme. This process has considerable merit, however a potential problem may be the relatively high maximum temperature required (925^{o}C). Further developments with the HTGR may increase the attractiveness of this cycle.

A process employing cesium and cesium oxides was patented by Miller and Jaffe in 1970 (Ref. 9). No experimental work was reported in the patent description. De Beni and Marchetti (Ref. 4) calculated, from available thermodynamic data, quite an unfavorable equilibrium constant for reaction 2. Consequently, in addition to the maximum high temperature required (1200^{o}C), this process would result in a considerable expenditure of work for separation and recirculation.

A small family of processes based on iodine exist. One such process, Catherine, is proposed by Wentorf and Hanneman (Ref. 6) at General Electric. It consists of six steps as shown. Reaction 1 is quite rapid at 80^{o}F, but the authors propose to allow it to run at 100^{o} to 190^{o}C so as to use the heat to evaporate liquid in other steps. Since iodine does not liberate oxygen directly from water in alkaline solution as does chlorine and bromine, the production of oxygen from iodine requires several steps. Also, it will be necessary to avoid undesired oxidation of iodide by excluding oxgyen in certain steps of the process. The authors calculate an overall efficiency of 64% (LHV) for the Catherine process.

Another process involving iodine has been suggested by Abraham and Schreiner (Ref. 10) at Argonne National Laboratories. It is a three step scheme which requires moderately low temperatures. The first reaction has not been tested, however since it is similar to the well studied oxidation of sulfurous acid by iodine to form hydrogen iodide and the sulfate ion, it is expected to go as indicated. The second and third reactions are well known.

A metal oxide process, based on tin, was suggested by Souriau in 1972 (Ref. 11). The author claims an overall efficiency of 36% (LHV) for this process, however a very serious drawback of this process is the extremely high temperature (1700°C) required for the second reaction. The author suggests that the temperature required for the decomposition of tin oxide be obtained from a nuclear heat source. This is impossible for current reactors.

Another process suggested by Wentorf and Hanneman at General Electric is the Beulah Process. In this process copper, chlorine, and magnesium are cycled through five basic steps. The last two steps are the same as used in the Agnes process for producing HCl and O_2 from Cl_2 and H_2O. A simplified flow chart for the Beulah Process has been developed and the authors calculate overall efficiency of 57% (LHV). The Beulah Process has a higher efficiency than the Agnes process because it operates at a higher maximum temperature and less heat is circulated internally.

The final process to be discussed is the Mark 2 processes proposed by De Beni. It is a three step cycle as shown. However, preliminary results from an experimental study of reaction one were not satisfactory. Consequently, work was stopped on this cycle to allow concentration on more promising schemes.

A.4.4 - Comparative Evaluation of Current Processes

It is premature at this point to attempt a rigorous comparative evaluation of the more than forty schemes proposed in the literature. In the first place, as indicated in the previous section, many of the suggested schemes are still in the conceptual stage. In other instances, experimental investigations of the equilibrium and kinetics of the various reactions are still in progress. Thus the degree of knowledge of the chemistry of the reactions is quite spread. And as the experimental work continues, it becomes more and more clear that existing thermodynamic data on many of these compounds are inadequate. Yields less than 10% the theoretical amount have been obtained (Ref. 5).

In addition to the lack of information on the yields and kinetics of reactions in currently proposed processes, new, and potentially better, schemes are under development. Hence the most promising thermochemical scheme may not have been proposed as yet.

Nevertheless, some general guidelines can be suggested when evaluating various processes. In general, the higher the highest heat input temperature, the higher the thermochemical efficiency. Since the capital costs and work of separation and recirculation will generally increase with the number of reactions in the process (proposed cycles generally have 3 to 5 reactions) the number of reactions in the process should be kept to a minimum (3 if possible). Also due to increased material and equipment costs, the use of highly corrosive materials should be avoided. Finally, the maximum temperature in the cycle should not exceed the temperatures from currently (or projected) available heat sources.

A.4.5 - Ultimate Potential

Hydrogen production by thermochemical processes employing nuclear heat sources has excellent potential to meet future hydrogen demands. While the majority of thermochemical cycles proposed to date are only in the early stages of development, the number of potential cycles is almost unlimited (Ref. 12).

This approach is aimed at competing with the electrolysis of water, since it employs nuclear heat as the primary energy source and water as the feedstock. The major advantage of thermochemical hydrogen production over electrolysis lies in the inherent potential of increased efficiency of conversion. And present indications are that there exists sufficient incentives for further development of thermochemical cycles. For example, recent studies have shown that high temperature (>1200°C) thermochemistry may be 20% more efficient than electrolysis, but at low temperatures (<650°C) this advantage is doubtful at best (Ref. 13). Nevertheless, even a few percent advantage would justify a considerable amount of research and development effort in this area.

The higher the maximum temperatures achieved in nuclear reactors, the greater the potential for nuclear water-splitting. Currently, the highest temperature nuclear heat available is from the HTGR's. However, nuclear reactors have been developed that operate at higher temperatures than HTGR's. The nuclear rocket propulsion reactors, developed in the Rover program, were designed and operated to heat hydrogen to temperatures around 2300°C for 10 hours (Ref. 14). And the UHTREX reactor was designed to heat helium to 1320°C and operate at fuel temperatures in excess of 1650°C for 30 days prior to project cancellation (Ref. 14). Both reactors used the same fuel technology (pyrocarbon-coated UC_2 beads) as the HTGR, but the core geometries were more finely divided, providing for smaller temperature differences between the fuel and the coolant. Thus, it is reasonable to expect, that with further fuel-technology development and with a different reactor core design, an HTGR type reactor could be developed to heat helium to higher temperatures.

Since the choice of any given cycle is dependent _a priori_ upon the availability of a heating fluid at a high enough temperature to supply heat to the endothermic reactions required, as the temperature of the heating fluid increases, not only does the efficiency of the reaction increase, but also the temperature range for possible additional cycles is extended. This allows a change in the chemical elements involved.

None of the proposed processes have been developed to the point where reliable cost estimates can be made. However, two sources indicate a hydrogen production cost of around $\$1.70/10^6$BTU (Ref. 14, 15).

One word of caution regarding the production of hydrogen from nuclear heat. "If all the transportation needs in the year 2000, i.e., automobile, air transportation, commercial and urban vehicles, and maritime, were to be satisfied by nuclear hydrogen it would be necessary to increase the projected nuclear electrical generating capacity by a factor of 2.0, which would represent a total investment in excess of $\$500 \times 10^9$. Obviously, it is unlikely that nuclear energy could be implemented to the required level at least not without

great effort, in the required time period" (Ref. 16). Fortunately, thermochemical hydrogen production need not solely rely on heat from nuclear fission, but may also employ solar, geothermal and (when developed) fusion energy.

A.4.6 - Research and Development Needs

Processes proposed to date are still at the stage of requiring further laboratory research to establish feasibility, yields and reaction kinetics. Since these processes are still in the proving stage, it is difficult to define a research and development program required to advance them to commercial practice. Clearly, however, a program should be established to yield a definitive evaluation of the potential of thermochemical hydrogen production. This program should include:

1. A continuing effort to develop new thermochemical schemes. Efforts here should include processes compatible with future higher temperature heat sources.
2. The development of criteria to screen existing and future proposed schemes.
3. An examination of existing thermodynamic data. Information to date indicates that some of the available data is inadequate, and it will be necessary to generate new thermodynamic and kinetic data for some classes of compounds to permit reliable evaluation of process feasibility and efficiency.
4. Greater attention to the potential of combined processes, e.g., chemical-electrolytic, for increased efficiency.
5. The development of thermochemical hydrogen production is coupled with the development of a sizable high-temperature primary energy industry. Therefore, fabrication techniques for fuel elements in nuclear reactors should be investigated

with the objective of designing a reactor core with a lower temperature difference between fuel material and coolant than is currently achieved (200-400^{o}C).

6. An investigation as to whether or not there exists the possibility of using the helium from the nuclear reaction directly in the hydrogen production unit. With this aim in view it will be necessary to estimate, in the context of a safety analysis, what constitutes the risks and consequences of the possible poisoning of the helium, following conceivable accidents in the plant.

7. A study of the design problems associated with a heat exchanger in a nuclear reactor-thermochemical system. Most likely it will not be possible to use the helium directly in the process and consequently the interface between the nuclear reactor and the water-splitting process will be a heat exchanger. Major areas where answers will need to be supplied to the nuclear reactor designers are:

   a) Process fluid - what effect will it have on the heat exchanger materials (primarily concerned about corrosion).
   b) Radiation stability of process fluid - since the fluid will not pass through the reactor core, and heat exchangers can be shielded by the concrete pressure vessel, neution activation will not be a problem. However, gamma radiation can deposit on the heat exchanger via particles carried by the helium from the core.
   c) Leaks - the consequences of a leak in the heat exchanger must be considered.
   d) Catalyst - if a catalyst is required for the process it may have a strong effect on the design of the heat exchanger, primarily because of removability or regeneration requirements.

e) Range of usable temperature for the process - this range establishes the core inlet temperature, which has a strong influence on the usability of present designs and materials. If the core inlet temperature should rise appreciably, say 100-150^{o}C above present values, then current thermal barrier parts, circulator parts, control rod drives, etc. must be redesigned and made of different materials.

A.4.7 - References

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A.5 - SUMMARY

Perhaps the most important single factor influencing the large scale use of hydrogen resides in the production system. It must be competitive to alternate, clean energy media, both in terms of the costs and the impact on the use of resources and the environment.

Clearly, our decreasing natural gas and crude oil reserves indicate that we cannot afford to continue producing hydrogen by the current practice of steam reforming methane and naptha, even to just meet the growing needs for use in ammonia production, oil refining, methanol production, etc. Appendix A discussed three options for the production of hydrogen: electrolysis, coal gasification, and thermochemical decomposition of water. Effort was directed towards determining the current status of technology, ultimate potential and inherent technological problems associated with these approaches. A summary for each of the hydrogen generation methods follows below.

Electrolysis

Production of hydrogen by electrolysis is the simplest and cleanest method for making hydrogen from water. An electrolytic cell operates with essentially no moving parts, can be designed to produce no by-products, and offers the physical separation of hydrogen and oxygen as well as the initial decomposition of water. In principle, cells can be operated at high pressure with no efficiency penalty, so that electrolysis also represents the most energy-conservative means of developing pressure in the hydrogen product.

Several large electrolytic hydrogen plants, consuming upward of 100MW, have been constructed and have operated successfully, while many thousands of smaller units are in use for special applications. However, because its primary energy source, electric power, is expensive and is only obtained at low efficiency (33-40%) from other energy sources, electrolysis is not a major process for hydrogen production.

The electrolytic process itself normally operates at efficiencies in the 60-75% range and at capital losts only a fraction (1/5 to 1/3) of the cost of the power station needed to drive it. Since electrolytic-hydrogen costs are dominated by electric-power costs, large electrolysis plants are located only where there is an abundance of cheap hydroelectric power. These plants have been optimized for low capital costs and normally operate at efficiencies lower than can readily be achieved in practice.

With the increase in power costs, more effort is being expended to develop the high efficiency potential of electrolysis. Present manufacturers anticipate an increase of overall electrolyzer efficiency to the 77-98% range within the next five years. However, various people and companies have considerably diverging opinions on the most favorable design concepts and technical approaches for electrolyzer construction, and there is no single type of electrolyzer that is universally held as superior.

Electrolytic production of hydrogen is an already achieved commercial process that can be improved considerably, both in capital cost requirements and in energy efficiency, by appropriate research. It appears that the various design philosophies proposed to date could result in hydrogen-generation techniques quite different in concept from each other, yet all of industrial significance in appropriate applications.

Coal Gasification

Coal gasification originated in the late 18th century. For about 150 years, it was a major source of town gas, industrial heating gas and of petrochemicals. The availability of natural gas at very low prices throughout the urban areas after World War II forced the closing of all but one coal gasification plant.

Coal, however, remains the fossil fuel of the future. The reason for this is its abundant supply which will last in the United States for at least 200 years. The other fossil fuels will be essentially depleted within 50 years.

There are two major processes of coal gasification currently used commercially: the Lurgi and the Koppers-Totzek processes. None of these processes are currently used in the United States but are well proven in many installations worldwide.

Within the next seven years, the Lurgi process is planned to be used in five coal to SNG gasification plants costing about 2.5 billion dollars. Hydrogen and carbon monoxide rich gases produced from coal will be converted in methanators to yield about 1.5 x 10 cubic feet per day of substitute natural gas. The Koppers-Totzek process is currently the preferred gasification process in applications when only hydrogen is required.

New processes of coal gasification are not expected within the next five years to make substantial changes in the presently used techniques of coal gasification. Future technology is moving towards a fluidized bed, high pressure gasification method.

Current preferred practice in production of hydrogen is steam reforming of petroleum products. The increases in the prices of crude oil and natural gas have not changed this practice. Uncertainties in cost and supply of capital and fuel stocks are apparently delaying a more extensive use of coal gasification by industry at large, with the exception of gas utilities where profits are guaranteed by the Federal Power Commission.

Thermochemical Decomposition of Water

The decomposition of water may be accomplished in a single, direct chemical reaction. However, this requires extremely high temperatures, greater than 2000°C. Heat sources capable of supplying this temperature are not readily available and thus it appears to be an impractical process for hydrogen production. Theoretically, however, by employing a process whereby in a series of two or more chemical reactions water reacts with an intermediate to form products that may be thermally decomposed to produce hydrogen and oxygen in separate reaction stages and regenerate the original

intermediate compound, hydrogen may be produced from water at much lower temperatures. In this scheme, the thermal energy in nuclear fussion reactors and nuclear fusion reactors, and solar and geothermal energy can be made directly available to the separation process.

While thermochemical processes to produce hydrogen are not in operation today, there is extensive research and development work in this area going on around the world. Most of this effort has focused on the thermochemical production of hydrogen employing a nuclear heat source.

In principle, thousands of combinations of multi-component closed-cycle chemical systems exist that might yield a workable thermochemical water-splitting process. Over forty schemes have been proposed in the literature to date, and there are strong indications that additional, very promising, processes have been developed that will not be published until patents have been received.

Processes proposed to date are still at the stage of requiring further laboratory research to establish feasibility, yields and reaction kinetics. As yet, none of these cycles have been proven experimentally, even at the bench scale. Thus, it is difficult to define a research and development program required to advance them to commercial practice. Nevertheless, present indications are that there exists sufficient incentives for further development of thermochemical cycles and therefore, a program should be established to yield a definitive evaluation of the potential of thermochemical hydrogen production.

APPENDIX B - HYDROGEN PIPELINE TRANSMISSION

ABSTRACT

In this study, a brief review of the natural gas transmission system is given and then the feasibility of utilizing regenerative turbomachinery as booster compressors on hydrogen transmission pipelines is examined. Requirements for hydrogen pipeline compressors extended as presently existing from the natural gas industry are examined. Performance factors, and problems of application are discussed and a review of regenerative turbomachinery literature is given. Technical problems which will arise when regenerative turbomachines are used to compress hydrogen gas are discussed and the possible solutions and design approaches which can be taken to overcome them are reviewed. An overall summary is provided of the state-of-the-art of regenerative turbomachinery.

APPENDIX B - HYDROGEN PIPELINE TRANSMISSION

APPENDIX B - HYDROGEN PIPELINE TRANSMISSION

B.1 - INTRODUCTION

It has been suggested that the natural gas pipeline system be employed for the transmission of hydrogen over long distance in this country (Ref.1, pg.B-2). Due to unique properties, problems in two broad categories are visualized if hydrogen were introduced. The first is the potential weakening of the pipeline itself due to hydrogen "embrittlement", especially at those locations where existing stress concentrations create the condition of plastic (as opposed to elastic deformation). This is not the subject of this report.

The second is the adverse effect on the existing pumping station machinery, both in performance insofar as ability to produce a sufficient pressure increase and flow rate in an efficient manner as well as operating lifetime; this is the issue considered herein.

The existing pumping station compressors--reciprocal in the older ones and centrifugal in the newer--are examined from the viewpoint of their expected performance with hydrogen vis-a-vis natural gas, and potential problems are identified in detail. The potential of a third type of compressor--a regenerative" compressor is examined for hydrogen pipelines. It is concluded that it could be far superior to the other two assuming that its efficiency and capacity can be increased beyond that demonstrated to date.

B.2 - NATURAL GAS TRANSMISSION

The natural gas transmission system in the United States comprised in 1970 some 914,830 miles of pipeline carrying 63.8 x 10^9 cu.ft./day of gas, representing an annual energy content of 23.34 x 10^{15} BTU. This energy distribution system served some 41,427,000 customers (op.cit.). A typical transmission pipeline is of the order of 36 inches in diameter and contains natural gas at 1000 psi and 60 ^oF, compressor stations are located approximately every 65 miles along the pipeline to boost the line pressure back up to 1000 psi from the 750 psi level

typical of the inlet pressure at the station. A compressor station may handle on the order of 500,000,000 cu.ft./day of natural gas.

The pumping machinery used in compressor stations has been multi-cylinder reciprocating compressors driven by natural gas engines. This type of machinery has been supplanted in recent years by two-stage centrifugal compressors driven by gas turbine engines/expanders. The reasons for this will be discussed further in a later section.

The composition of natural gas from various locations in the United States is shown in Table B.2-1 taken from Ref. 2 the principal component is seen to be methane. Of interest to note is the wide variation in composition of natural gas from different locations. Comparison of properties of methane with those of hydrogen appears in table B.4-1.

TABLE B.2-1 - COMPOSITION OF NATURAL GAS AT WELLS

Location	Methane	Ethane	Higher HC	Nitrogen	CO_2	Other
Alaska	98.9	0.2	---	0.7	0.1	0.1
California	82.4	7.7	8.6	0.5	0.8	---
Colorado	68.0	7.2	5.9	18.2	0.1	0.6
Kansas	78.1	6.1	5.0	10.0	0.2	0.6
Montana	79.9	8.5	4.6	4.5	2.3	0.2
New Mexico	72.9	11.0	12.1	3.5	0.2	0.3
Ohio	86.8	5.9	3.3	3.6	0.2	0.2
Oklahoma	85.0	6.7	6.4	1.5	0.2	0.2
Pennsylvania	97.1	2.0	0.1	0.5	0.1	0.2
Texas	81.6	6.5	3.8	7.7	0.1	0.3
Texas	91.8	4.5	1.8	0.5	1.3	0.1
Utah	42.0	8.0	7.5	15.2	25.8	1.5
West Virginia	75.3	14.2	9.3	0.8	0.2	0.2
Wyoming	86.2	7.8	4.1	0.3	1.5	0.1
Australia	95.6	0.3	1.4	0.8	2.0	---
Canada	88.5	2.5	2.6	6.2	0.2	---
Venezuela	73.7	13.8	10.3	---	2.2	---
Transmission Line Linden, N.J.	94.5	3.3	1.2	0.3	0.7	---

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B.3 - PIPELINE COMPRESSORS

Before an appropriate compressor type can be selected for a particular application, certain basic information relating to its performance requirements should be at hand. This includes: pressure ratio, flow rate, efficiencies desired, and could include other special characteristics, as for instance avoidance of pulsations or gas contamination by lubricants. Long life and low maintenance requirements (especially at remote stations) are also usually desirable. One can then consider the type of machine desired from the range of types of compressors available, shown in Figure B.3.1. In this figure is shown the division of compressor types into the two broad categories of positive displacement machines which increase the pressure of a gas by confining it in a decreasing volume, and dynamic machines which operate by imparting kinetic energy to the gas which is then converted into pressure rise by diffusion. These latter machines utilize one or more rotating impellers and diffusor passages to achieve this. Not shown in this figure are devices which raise the pressure of a gas by mixing it with a previously pressurized modium. (ejectors). Further differentiation of compressor types is also given in the figure.

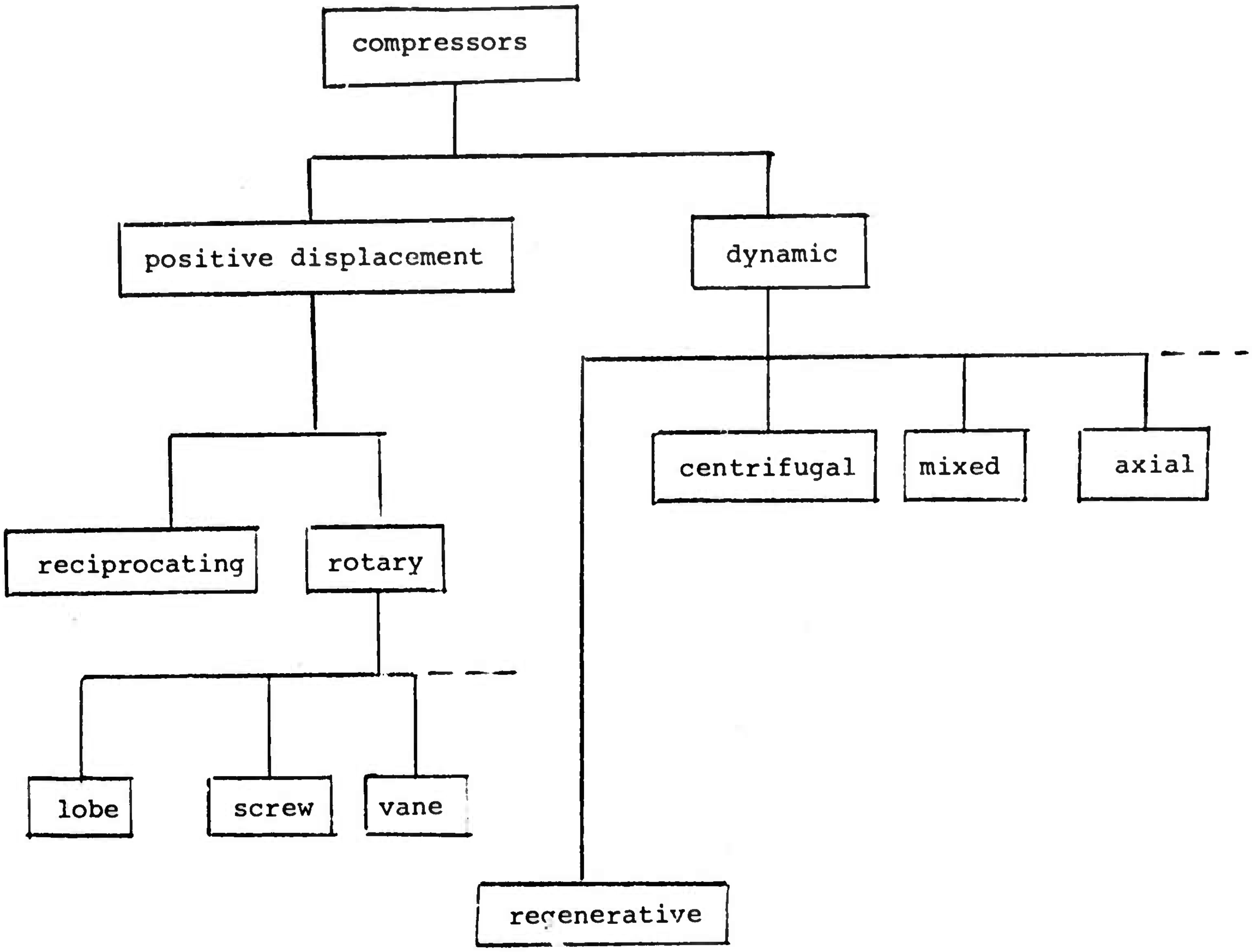

FIGURE B.3-1: COMPRESSOR TYPES

One common way to categorize compressors as an aid to selection for a given application is in accordance with the specific speed, N_s, which combines the pressure ratio, capacity and a characteristic speed into a dimensional grouping as follows:

$$N_s = \frac{N\sqrt{Q}}{H^{0.75}} \qquad \text{(B.3.1)}$$

where N = characteristic speed

Q = capacity

H = pressure rise

On this basis the range of compressor types proceeds from positive displacement compressors, at low specific speed, through centrifugal and on to axial flow compressors at high specific speed. By examining the efficiency variation with specific speed for each type of compressor, a rational partial selection within overlapping ranges of specific speed may be made. It should be noted that this parameter (N_s) is most meaningful when applied to dynamic machines. Further compressor types can be found in References 1-3. Information on a more detailed discussion of efficiency - specific speed variations for centrifugal machines appears in a later section of this report.

B.3.1 References

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B.4 - HYDROGEN TRANSMISSION

Before examining the question of hydrogen pipeline transmission and the related compressor requirements, it will be illuminating to examine the types of machines now used in natural gas transmission.

At present in the natural gas industry two major types of compressors are used to boost the pressure along the pipe lines. These are reciprocating compressors (piston type) and centrifugal compressors. The latter machines have largely supplanted the

former in pipeline service, due to the following reasons:

a. An increase of capacity of pipeline systems and steadier operating conditions which led to:

b. Lower pressure ratios and closer spaced compressor stations. Following this:

c. Lower initial cost and maintenance expense were experienced for centrifugal compressors.

If the pipeline will be handling hydrogen instead of natural gas, several problems arise with both types of machines due to the difference in properties of hydrogen and natural gas, summarized in Table B.4-1 below:

TABLE B.4-1: PROPERTIES OF HYDROGEN AND NATURAL GAS

Chemical formula	H_2	CH_4
Specific gravity, $0^{o}C$, 700 mm Hg	0.08987	0.7169
Molecular weight	2.016	16.032
Ratio of specific heats	1.41	1.30

These problems will be discussed further in a later section but are briefly mentioned below:

a. Both designs will suffer to one degree or another from hydrogen environment embrittlement depending on the materials chosen for the design.

b. Reciprocating compressors will have a serious sealing problem due to the rapid diffusion of relatively small H_2 molecules and the attack by H_2 on sealing materials in non-lubricated designs.

c. Centrifugal compressors will not produce the required pressure ratios without extensive multi-staging; since pressure rise is the product of density and head rise, a lower density gas requires a higher head machine.

Furthermore, both machines will have to be built in expanded capacities to deliver the same energy content with hydrogen as they carry with natural gas, since only 26% of the present energy capacity at 750 psi with methane will be delivered when handling hydrogen (Ref.1), due to the lower density of hydrogen.

An example of a reciprocating compressor design now used for a natural gas transmission which might be used to handle hydrogen is shown in Figure B.4-1, taken from Reference 2; examples of a

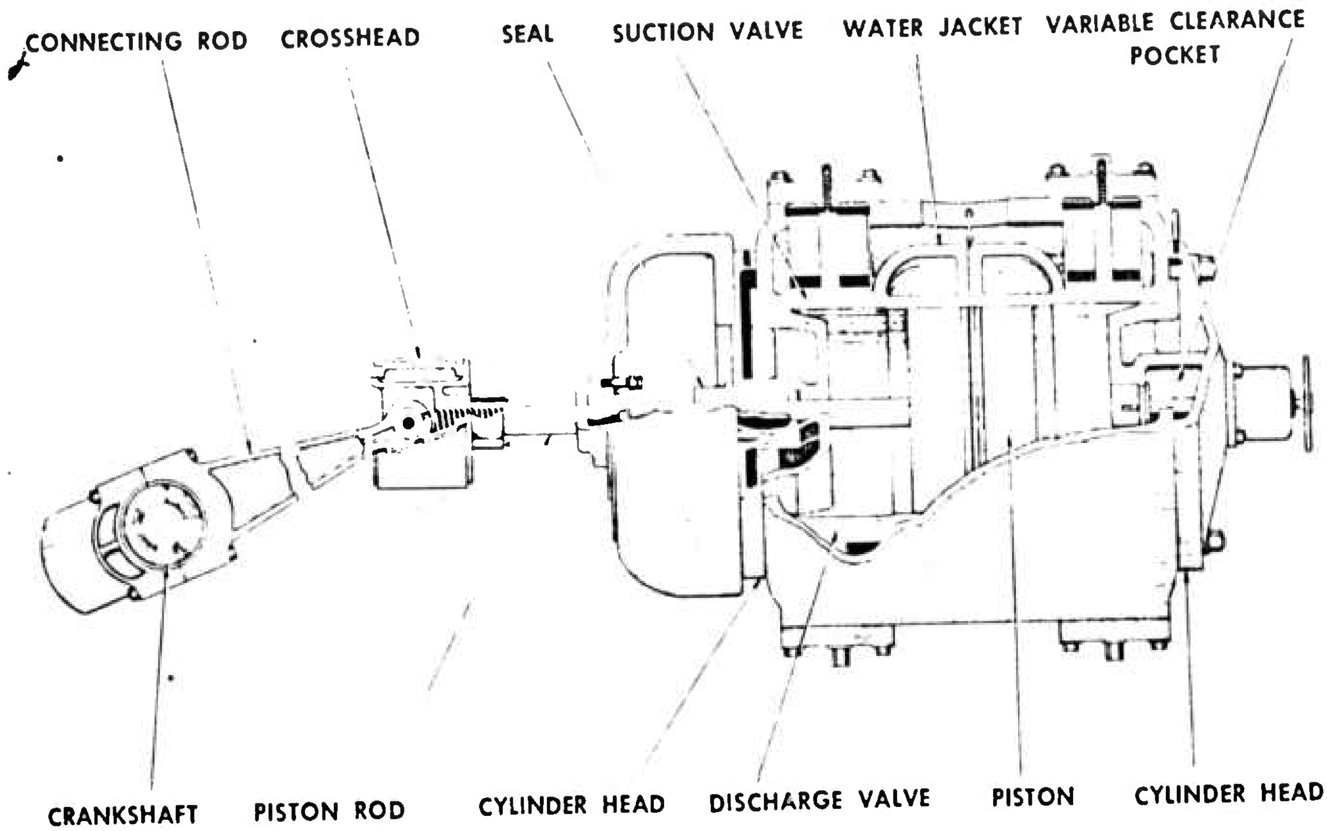

Figure B.4-1: Reciprocating Compressor for Pipe Line Service (Rexnord, Inc.)

centrifugal compressor design presently used to handle natural gas and a multistage design which might be used to handle hydrogen are shown in Figures B.4-2 and B.4-3. It is worth noting that in 1972, the installed compressor station horsepower exceeded ten million, (Ref.3). The centrifugal machine has largely supplanted the reciprocating machine in natural gas pipeline service for the reasons previously discussed. However, in handling hydrogen, design difficulties arise in generating the required pressure rise (head) with centrifugal machinery and it becomes necessary to go to a multi-stage compressor in order to achieve the head required for a minimum of compressor stations along the pipeline, or to consider another type of compressor, to be discussed in the next section of this appendix.

Before leaving this section, however, it is of interest to denote that there has never been any hydrogen pipeline system developed to the point where compressor stations have been necessary. The most developed hydrogen pipeline system is in Germany and comprises some 130 miles of steel pipe, twelve inches in diameter distributing hydrogen gas generated at 600 psi. The gas simply blows down the pipeline and is delivered to users at 225 psi. Details of this pipeline system can be found in Ref. 4. There has been some hydrogen compressor design and development experience to date, mostly related to liquification and process work. No such design or development experience appears to exist on the scale required for pipeline application.

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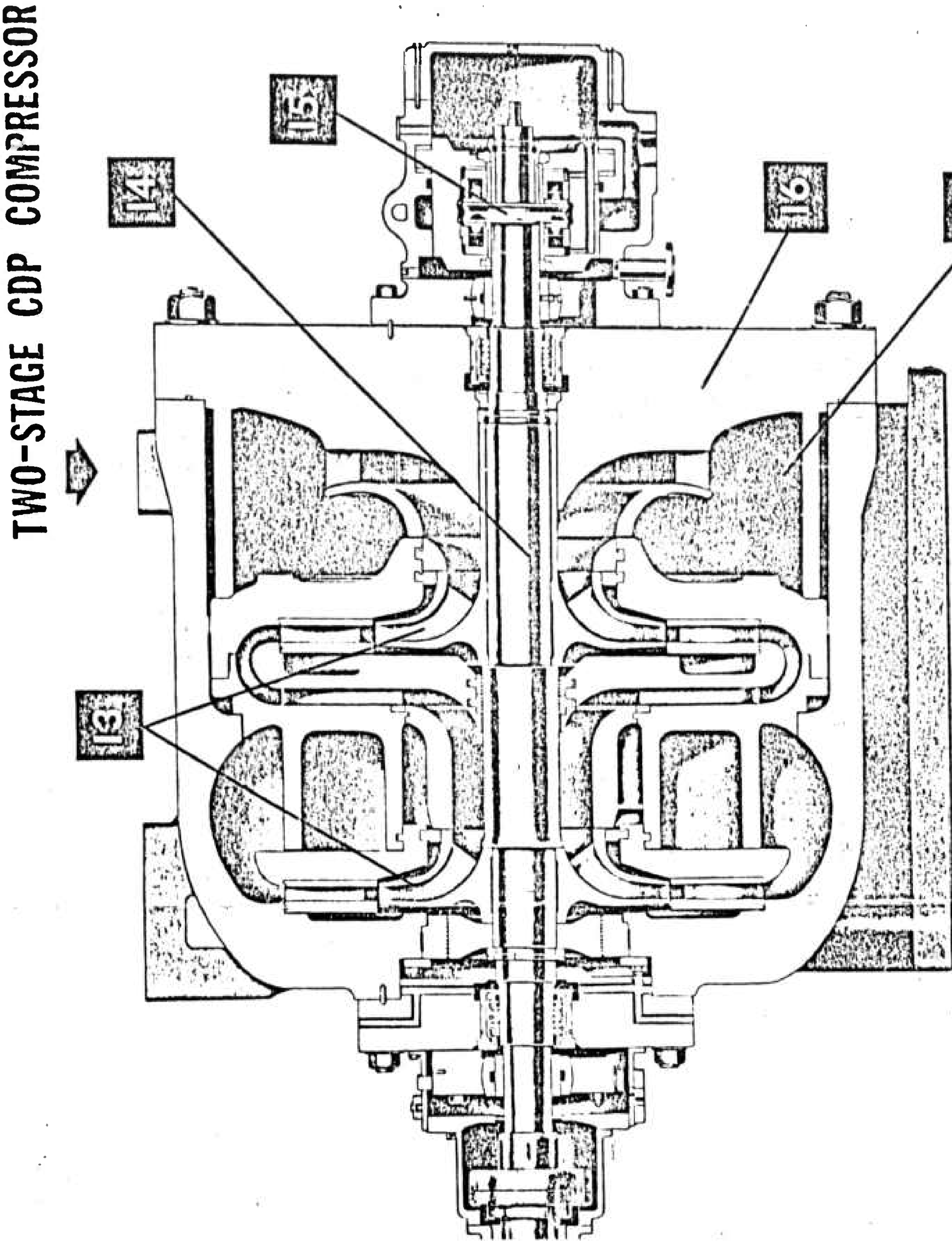

Figure B.4-2: Centrifugal Compressor for Natural Gas Service (Ingersoll-Rand Company)

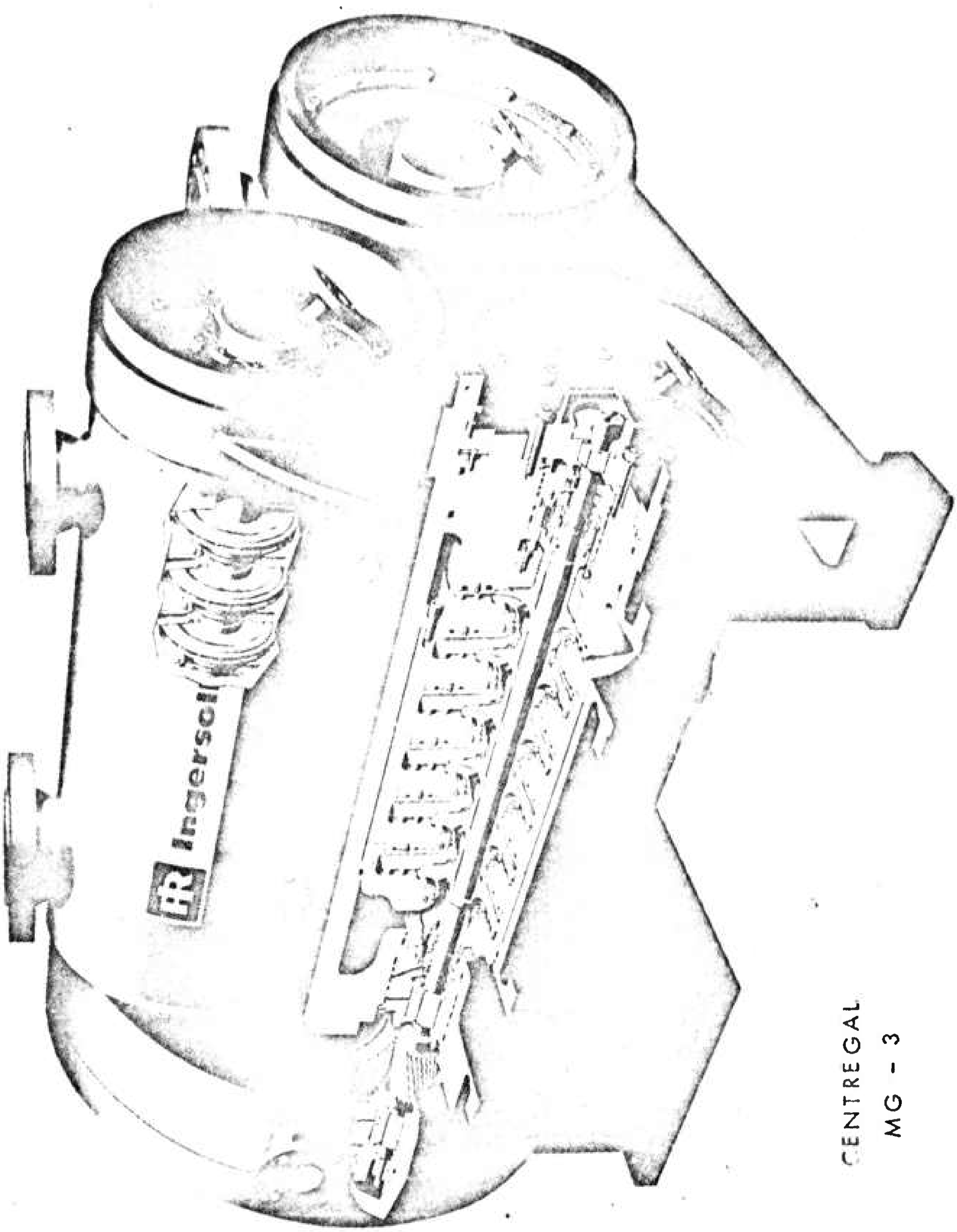

Figure B.4-3: Centrifugal Compressor for Hydrogen Service

B.5 - REGENERATIVE COMPRESSORS

A possible solution to the design difficulty discussed in the last section is to utilize the regenerative compressor for hydrogen gas pipelines. "Regenerative" compressors are capable of making the head in a single stage that would normally require seven to eight centrifugal stages. This is because the head coefficient* obtainable from this type of machine is of an order of magnitude higher than that obtainable from a centrifugal machine. However, regenerative machines have been efficiency limited until very recently and have also been generally applied in the low end of the centrifugal compressor specific speed range. Figure B.5-1 shows a fairly conventional regenerative turbomachine. We see the construction of a multi-blade impeller with open side channel on one side. A barrier in the side channel between the inlet and outlet ports causes the establishment and maintenance of the regenerative flow pattern. As the impeller rotates the fluid circulates in and out of the blade buckets several times during one revolution gaining energy with each reentry. This type of flow pattern allows the generation of high pressure at low rpm.

Assuming a conservative design point head coefficient for a regenerative machine of 3.5, (this design point head coefficient is of the order of five times higher than a comparable design point heat coefficient for a high speed single-stage centrifugal machine), we see in Figure B.5-2 the head which can be made with a regenerative machine at various speeds of rotation for various diameter impellers.

The efficiency limitation of regenerative turbomachinery is shown in data presented in Figure B.5-3 giving the comparative efficiency of low specific speed pumps of centrifugal, Barski, regenerative and advanced regenerative designs (Garret) as a function of specific speed. It can be seen that the regenerative

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* Head coefficient is the ratio of the pressure rise produced by an impeller to the square of the tip speed. When taken at the design point (maximum efficiency) it is usually referred to as the design head coefficient. The pressure rise produced by a dynamic compressor is a function of the head rise and the density of the gas.

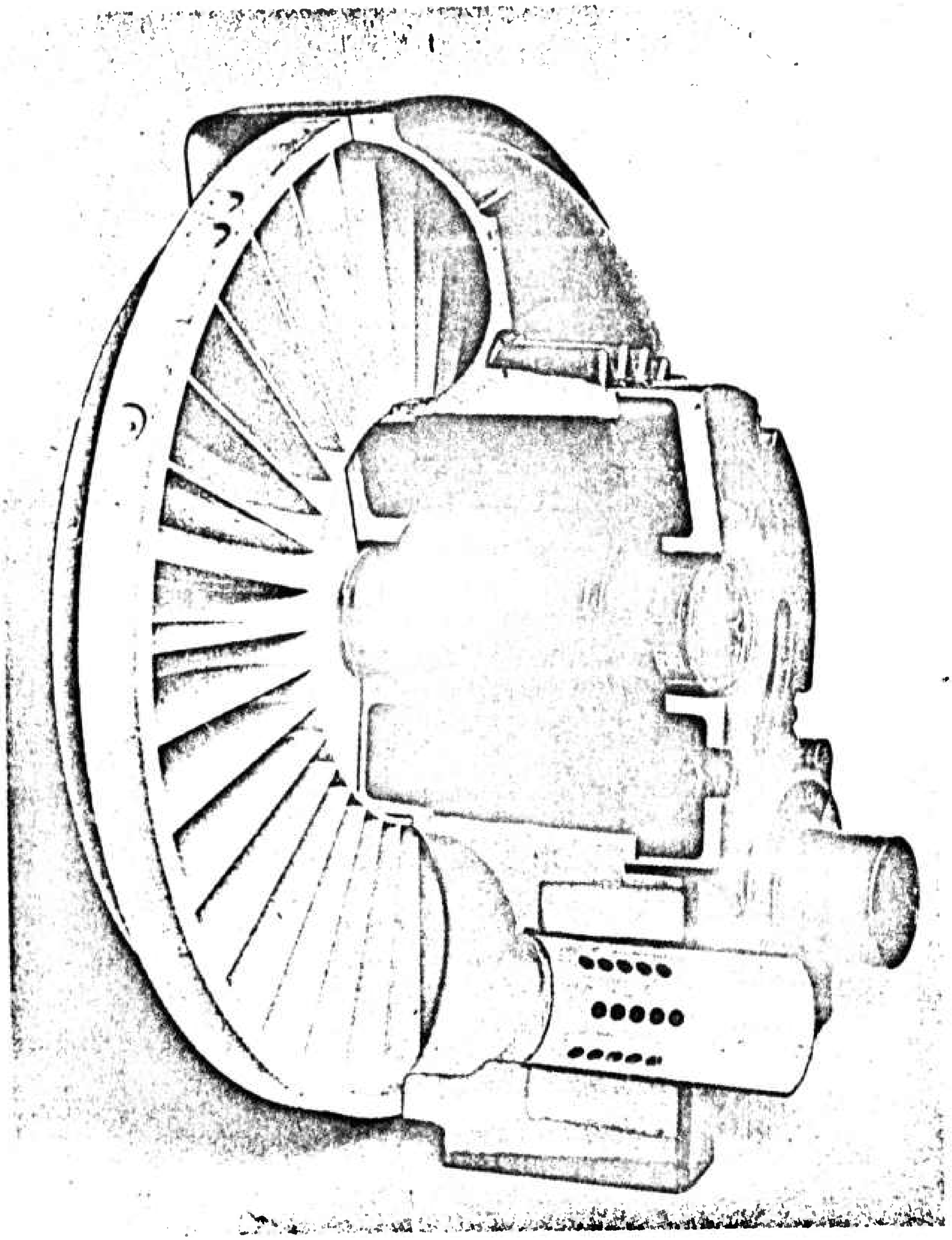

Figure B.5-1: Regenerative Turbomachine (Singer)

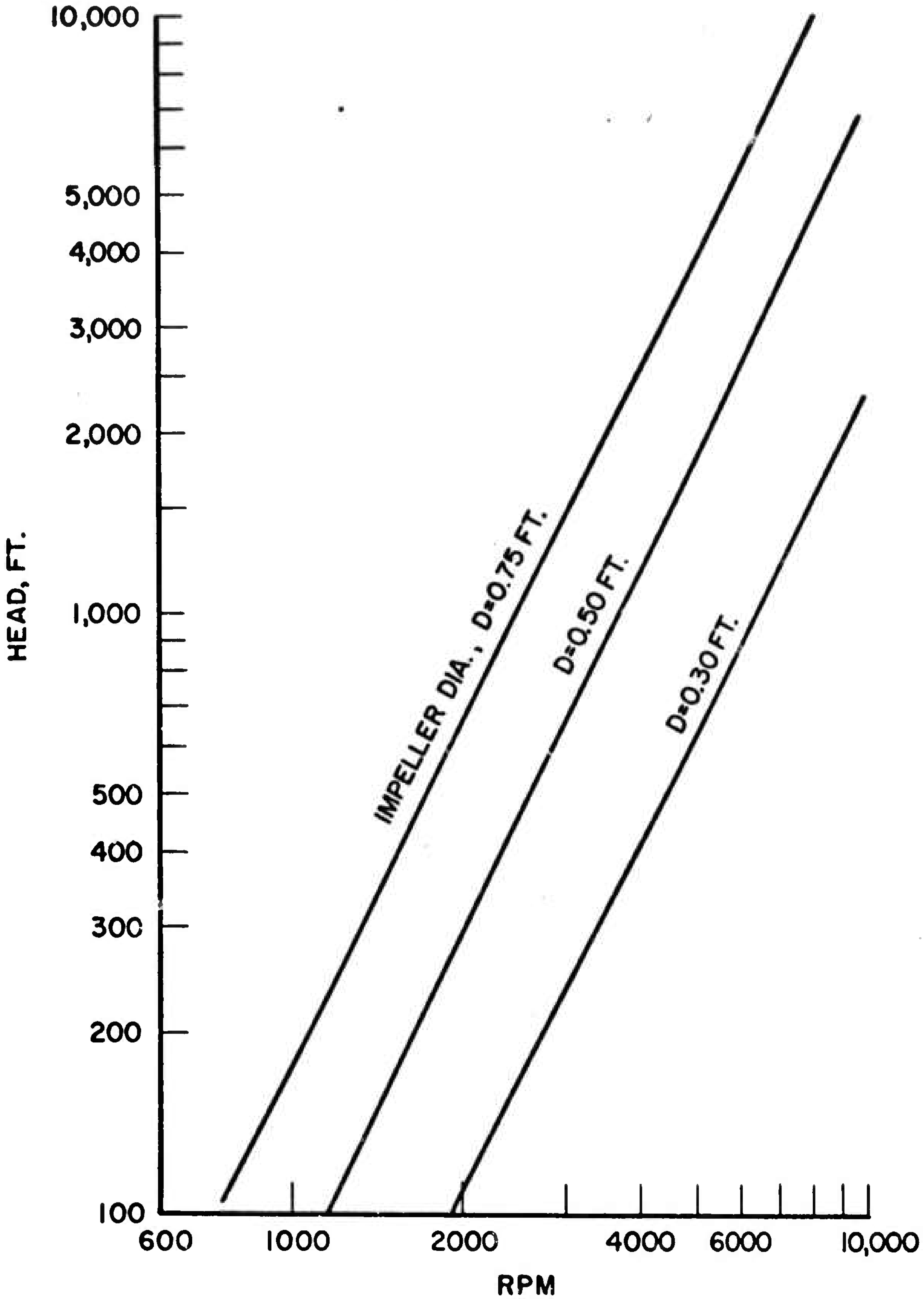

Figure B.5-2: Regenerative Turbomachine Head-Speed-Size Performance

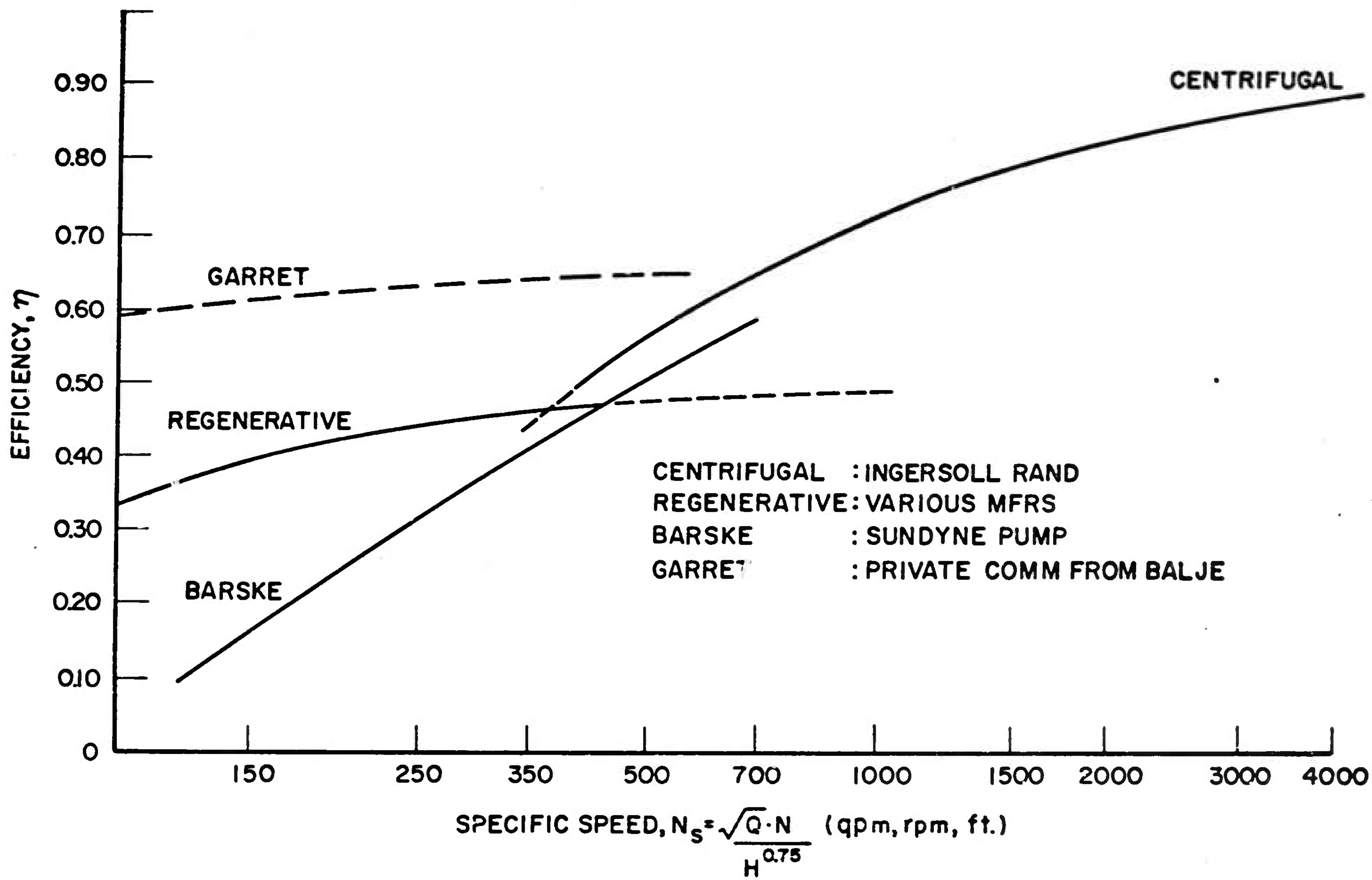

Figure B.5-3: Comparative Efficiency of Low Specific Speed Pumps

machine has tended to peak at about 50% efficiency in the low specific speed range, while the centrifugal picks up from this point. Also it can be noted that in very low specific speed ranges the regenerative is more efficient than the centrifugal.

Recent developments carried out at Garret Company based on earlier work at Sunstrand Corporation carried out by Dubey under government sponsorship* have shown that it is possible to substantially improve the efficiency of regenerative turbomachinery by the improvement of the ordering of the flow pattern in the side channel, reduction in the extent of impeller blading and better aerodynamic design of the bladed elements. The improvement in efficiency obtainable is shown in Figure B.5.3. Figure B.5.-4 shows a diagram of this improved type of regenerative turbomachine. It now becomes possible to contemplate the use of this design on hydrogen pipeline service, where high horsepower designs are needed.

The next section of this report will review the literature and historical development of regenerative turbomachinery and bring us to the point where we can examine the application of the improved regenerative machine for compressing hydrogen gas in pipeline service.

B.5.1 - Literature Review

The regenerative turbomachine appears to have originated in either Germany or Holland shortly after the First World War. It was the subject of a number of Doctoral Theses at German Technical Universities during the period between the wars. Among these are the thesis of Carl Ritter (Ref. 1) at the Technische Hochschule of Dresden, the thesis of Walter Schmeidchen (Ref. 2) also at the Technische Hochschule of Dresden, the thesis of Carl Schmidt (Ref.3) at the Technische Hochschule of Hannover and the thesis of Heinrich Engels (Ref.4) at the Technische Hochschule of Hannover. These earlier investigators were concerned with exploring over a wide range, the effects of varying

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* see references, B.5

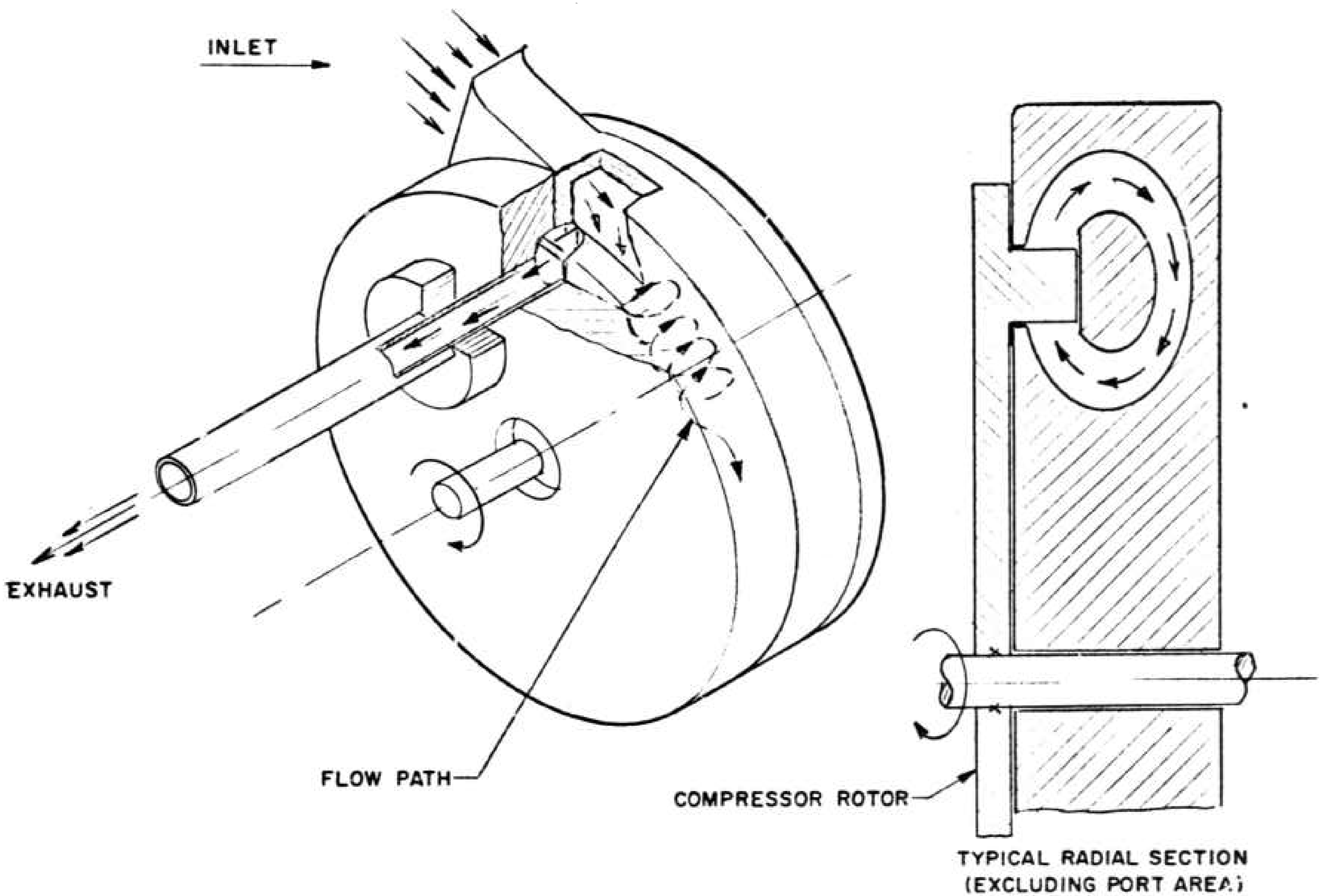

Figure B.5 4: Advance Design Regenerative Turbomachine (Ref. B.5-6)

geometry on the design of regenerative machines. The experiments involved work varying the proportions of blading to coverage of the side channel over the blading, shape of side channel and blading and the like. As a result of these investigations, a great deal of information was derived allowing one to reach the optimum proportions for conventional regenerative turbomachinery design. These efforts have been summarized in a book by Pfleiderer (Ref. 5).

Of special interest is the work of Engels dating from 1940 in which he not only concentrated on the circular radial section for impeller and side channel but also introduced the concept of a guiding ring (which turned out to be the concept used by Silvern (Ref. 6) in his research at Sunstrand) in order to better guide the flow and reduce the chaotic mixing process, thereby raising the efficiency level. However, in Engel's work the ring was attached to a full-bladed impeller and rotated with it, which limited its effectiveness. This point will be further discussed later.

Other investigators, following the Second World War, picked up this early work and attempted to develop a rational theory for the type of flow developed within the regenerative machine. One school of thought, the leading exponents of which were Crewdsen (Ref. 7) and Iversen (Ref. 8) postulated the essential flow mechanism as being one of drag induced by the impeller on the stationary fluid in the side channel. Certain explanations of observed performance were obtainable by means of this hypothesis which however, proved to be limited in explaining many of the other features of performance which were observed.

Work was also carried out at Massachusetts Institute of Technology (Ref. 9), National Aeronautics and Space Administration (Ref. 10), and Oak Ridge National Laboratory (Ref.11). The interest at the latter location being one, significantly enough, of utilizing the regenerative machine as a light gas compressor and circulator in the gas-cooled reactor designs which were being developed there. Mention may also be made of the work done by Shimasaka (Ref.12) and Senoo (Ref.13) where the

emphasis was on the development of the regenerative turbomachine as a pump where its low NPSH* performance characteristics are attractive.

Recent investigations at Universities have included work by Burton (Ref. 14) and Grabow (Ref.15) where attempts were made to define and develop further the theory upon which a rational design approach to this type of turbomachine could be made. In addition, there were investigations directed toward utilization of this type of turbomachine as a turbine. Emphasis in this area was given in research conducted by Balje (Ref.16)

In the meantime, commercial development of this type of turbomachine continued, principally as a pump in Germany and elsewhere in Europe and in the United States as well, where its high head, favorable low NPSH characteristics allowed it to enjoy a special application advantage and where its efficiency limitations were not especially important. This latter factor however, tended to limit the sizes in which this type of machine was built and sold to less than 50 horsepower. This is two orders of magnitude lower than the horsepower requirements of a typical compressor station on a natural gas pipeline.

In the last 15 years, the machine has begun to be developed as a gas handling device. First, as a high pressure blower (Ref. 17,18) and more recently moving into the range where compressors would normally be applied. Again, this work was pioneered in Germany but has been picked up in the United States and is actively under development at this time in several locations. Among these, may be listed, Garrett Corp. in California; Rotron Manufacturing Co. in Woodstock, N.Y.; and others.

This brief review, it is hoped, has served to point the direction in which development of this type of machine is occurring, and to lend support to the concept that it may well be a suitable machine to apply for the purpose of compression of hydrogen gas in pipelines. This point will be discussed in more detail in the next

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* NPSH, or net positive suction head is a term usually taken to signify the pressure available at the pump inlet above the cavitation pressure at that point.

section of this report.

B.5.2 - Technical Problems

This section and the next will be devoted to a discussion of the technical problems which will have to be faced in applying the regenerative turbomachine for the compression of hydrogen. These fall into groups as follows:

(a) the need to raise the efficiency levels of the machine to those levels which are now enjoyed by centrifugal compressors;

(b) the need to extend the range of specific speed to higher values than those where the machine has been applied before;

(c) the need to eliminate the noise which the machine will generate at the blade passing frequency at high sound pressure levels, due to the close running clearances between impeller and casing port barrier.

(d) the need to provide adequately for the somewhat peculiar loads that the impeller will throw onto the shaft and bearings as a result of the regenerative turbomachine geometry;

(e) the need to choose proper alloys or other means to avoid hydrogen embrittlement. This difficulty is shared with other compressor designs

B.5.3-Possible Solutions, Design Approacnes, Recommendations

The technical problems which were raised previously may be approached in a number of ways which will now be discussed corresponding to the order in which they were raised in the previous section.

(a) It may be possible to raise the efficiency of regenerative machinery beyond the levels which have been obtained thus far by means of improving flow guidance in the side channel through proper proportioning of the turning ring and channel geometry in relation to the blading so that the diffusion process occurs in a more guided manner. Another approach suggested by F. Sisto* would be to utilize the turning ring itself which can be made hollow, as a heat exchanger so that the compression may approach the isothermal condition; that is circulate a coolant through the hollow turning ring and reject the heat of compression outside the machine via an auxilliary heat exchanger.

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* private communication

(b) The range of specific speed may be extended; that is it may be possible to apply the design to a higher flow rate through improvement in the inlet and outlet porting creating a better match to the blading geometries. As a side benefit, this may also contribute to the raising of efficiency if the inlets and outlets can also be designed to provide some turning for the flow. The extent to which this may be achieved is unknown at this time.

(c) Noise problems may be approached through two basic means: first, tuned silencers may be provided at the inlet and outlet of the machine designed so that maximum attenuation occurs at the blade passing frequency. These silencers can also be designed so as to provide some attenuation for broad band or aerodynamic noise as well. In addition, it may be possible to reduce the noise level of the machine through staging, that is dividing the total work among two or more impellers although this may increase the complexity of the machine to a certain degree. It may also provide a benefit with respect to accommodating the loads developed on the impeller and transferred to the shaft and bearings.

(d) The bending and twisting loads that a regenerative impeller develops tend to cause the impeller to rotate in a plane not perpendicular to the shaft. This creates problems in maintaining a uniform clearance between the impeller and the casing port barrier, and also contributes to unbalance and reduction of bearing life. One way in which it becomes possible to solve this problem is by staging where the impellers are arranged so that the net eccentricity developed is reduced to zero. It also is possible to design impellers with double-sided blading and to arrange the inlets and outlets in stages in a multi-stage design alternately around the periphery of the casing. One should also try to provide as large a bearing as possible, particularly in overhung designs at the impeller end of the shaft.

(e) The problem of embrittlement in a regenerative compressor will be in many respects similar to that experienced in other types of compressors with the exception of the following: the impeller itself because of its geometry can be fabricated from castings or forgings essentially in one piece; therefore, stress raisers that may exist in fabricated centrifugal impellers due to welded construction are eliminated.

B.5.4 - References

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B.6 - SUMMARY

If hydrogen comes into widespread use as a synthetic fuel, large scale pipeline transmission of gaseous hydrogen across the United States will be necessary. Compressor stations along these pipelines will be required to periodically boost the pressure as is now the practice in the natural gas industry. Existing compressor station designs can be adapted for hydrogen service, but at an increase in complexity and overall operating costs together with a loss of simplicity and reliability. Utilization of regenerative turbomachinery as a hydrogen pipeline compressor offers a way to maintain the advantage, experienced by the centrifugal compressor in natural gas pipeline service, as reviewed previously.

The regenerative compressor can also be used as a natural gas pipeline compressor; in fact, it can be designed to handle both natural gas or hydrogen or any mixture of the two. Further, it may be possible to accomplish this in a single design which can be adjusted to handle a varying mixture by speed control or other means. In either case, the regenerative compressor will have to be a new design; taking advantage of the latest technology.

Technical problems will exist in applying the regenerative turbomachine in this area but the historical trend in the development of this machine suggests that these technical problems can be resolved and that the regenerative compressor may take its place in hydrogen pipeline service maintaining the advantage obtained from present day centrifugal compressors on natural gas service.

APPENDIX C - HYDROGEN-FUELED ENGINES

ABSTRACT

The use of hydrogen (H_2) as a fuel for spark-ignition, reciprocating engines was investigated as part of a continuing program. Engine performance parameters (e.g., specific fuel consumption, power output, mean effective pressure, etc.) are related to fuel properties (e.g., chemical energy, molecular weight, etc.) analytically via a series of equations that involve the indicated thermal efficiency. Based on fuel-air-cycle approximations, values of indicated thermal efficiency (and the concentration of the oxides of nitrogen generated) are obtained and the performance parameters are evaluated for H_2-fueled and gasoline-fueled engine operation; illustrative calculations are presented.

Operating experience with H_2/air and other hydrogen-fueled reciprocating engines is reviewed with emphasis on thermodynamic performance and pollutant emissions. Experimental data are evaluated in light of the performance-parameter analysis. Performance is seen to suffer from decreased full-load output unless appropriate fuel injection or supercharging is used; efficiency and pollutant-emission gains are attractive at part-load operation via quality (i.e., mixture-ratio) control. Further analytical and experimental data are required, however, for a comprehensive evaluation of potential, particularly as regards fuel-injection.

APPENDIX C - HYDROGEN-FUELED ENGINES

APPENDIX C - HYDROGEN-FUELED ENGINES

C.1 - GENERAL INTRODUCTION

It appears that H_2 was first suggested as a fuel for an engine by the Rev. W. Cecil in 1820 (Ref. 1). Commercial operation of trucks fueled by H_2 was demonstrated over 50 years ago (Ref. 2). Systematic laboratory investigation of its characteristics in a spark-ignition, reciprocating internal-combustion engine was first reported 50 years ago as well (Ref. 3).

Since then it has become a major fuel for liquid propellant rocket spacecraft (Ref. 4) and has been used to power aircraft gas turbine engines (Ref. 5). Its use in subsonic transport planes could materially increase the payload achieved with hydrocarbon fuels or materially increase the range of supersonic transport planes. It has been proposed as the fuel (Ref. 6) that could simultaneously end automotive (Ref.7), aircraft (Ref. 8) and other combustion-generated pollution of the environment, as well as become the principal energy transport medium of the future as the earth's petroleum resources are depleted (Ref. 9). However, in making a decision on the use of H_2 vis-a-vis other possible fuels it is important to have knowledge of their comparable performance, for example, the efficiency with which the chemical energy is converted into mechanical work (Refs. 10,11).

C.1.1 - Scope of Appendix C

This appendix is largely restricted to ordering and summarizing both fundamental considerations and operating experiences with H_2-fueled piston engines, reciprocating and rotary. Rocket engine experience is outside the scope of the present program. Although, some of the fundamental considerations apply to gas turbines as well as piston engines, gas-turbine operating experience with H_2 as a fuel has not yet been sufficiently reviewed to warrant inclusion of this type of engine in this document. It is planned that the Second Semi-Annual Technical Report will extend the depth

of treatment of piston engines and breadth of coverage to other H_2-fueled engines, notably gas turbines.

In Section C.2, "Fundamental Considerations", basic performance parameters are defined and discussed in the light of the peculiarities of H_2 as an engine fuel. This section serves to clarify some of the prospective advantages (e.g., efficiency, "quality control" of power) and disadvantages (specific power, torque) anticipatable in H_2 use as a fuel, particularly in piston engines. Section C.2 also includes illustrative calculations aimed at putting hydrogen in perspective by comparing it roughly with gasoline as a piston-engine fuel. Finally, Section C.2 serves as background for the summary and discussion of prior operating experience with hydrogen in both air and oxygen-breathing piston engines.

Section C.3, "Reciprocating Engines: Summary & Evaluation of Operating Experience", orders and summarizes the data available from previous and current operations with hydrogen-fueled piston engines. Some tentative conclusions are reached regarding overall performance; some value judgements must, however, be postponed pending further analysis and experimentation on H_2-fueled engines.

C.1.2 - On Relating Fuel Properties to Engine Performance

Excepting rockets, by far the greatest operating experience from H_2-fueled engines of any class has come from experiments on positive-displacement engines. Positive-displacement engines as a class include reciprocating and rotary-piston engines in which the quantity of working fluid (e.g., combustion products) in the engine is at some point(s) in the engine process completely enclosed by solid boundaries (thereby filling a well-defined,closed volume).

Of all positive-displacement engines, air-breathing, reciprocating, spark-ignition, Otto-cycle engines have been most extensively tested. However, all such engines which have been H_2 fueled were of designs developed and in varying degrees optimized (over decades)

for use with gasoline as a fuel. Only minor modifications were made in adapting these engines to H_2 operation; they are still "gasoline engines" when operated with hydrogen. Such engines cannot be considered to have been transformed into "hydrogen engines", optimized for the use of H_2. Thus, operations with H_2 as a fuel in a gasoline engine are at a congenital disadvantage vis-a-vis gasoline operation, and comparisons are inherently biased against hydrogen as a fuel. However, there is no simple alternative and therefore, herein as elsewhere, such comparisons are made.

In order to explain, predict, or otherwise rationalize engine performance data, it is necessary to relate these data to fuel properties. Fuel properties are introduced explicitly in Section C.2 in relationships between efficiency and other performance parameters such as power output, mean effective pressure or torque, specific fuel consumption, etc. Implicitly, fuel and combustion-product properties also determine efficiency.

The fundamental explicit performance relationships are developed in Section C.2 in a form which shows the influences of the chemical energy of the fuel, its molecular weight, etc. This clarifies some of the influences on engine performance of hydrogen's unique properties.

Implicit influences of fuel properties on engine efficiency can be seen in the empirical test data of Section C.3. A classic basis for doing this is by comparing experimental efficiencies with those from analysis of a model idealized engine operation. The fuel/air-cycle approximation has been commonly used as the model for approximating and comparing with the experimental performance of gasoline Otto-cycle engines. In the case of hydrogen engines, however, a search of the literature has revealed such calculations for only two isolated operating points. As part of the present effort, a computer program has been written to make additional calculations, but these have not yet been made. For the present purposes, then, Section C.3 compares experimental efficiency data with the two fuel/air-cycle calculations which are available in the literature and with one additional result calculated "by hand" as part of the present program.

C.2 - FUNDAMENTAL CONSIDERATIONS

The purpose of this section is to show the relationship between fuel properties and engine performance parameters. Analytic expressions are used whenever possible. Since piston engines are the main concern of this report, the equations will be so specialized. They can be used as a basis for the evaluation of H_2 as a fuel, for comparison of H_2 with gasoline or other hydrocarbon fuels, and for rationalization and evaluation of actual engine experience reported on in Section C.3.

The difference between work (or power) produced on the piston and that which appears on the shaft is due to mechanical losses. These are not of concern here, so attention will be focused on piston work, i.e., that produced by pressure in the cylinder. Such quantities are designated as "indicated" quantities, i.e., indicated thermal efficiency, indicated mean effective pressure, etc. and are directly influenced by fuel properties. They are used to report engine performance when the purpose is to relate it to fuel properties, including their combustion processes. However, as discussed in Section C.3, there are examples in the literature where shaft (or "brake") work (or power) is reported without sufficient information (i.e., friction work or friction power) to correct the shaft quantities to indicated quantities. Thus, they are of very limited utility for the present purpose.

The most important engine-performance parameter -- it appears explicitly in the equations for all of the others -- is the efficiency of conversion into work on the piston of the fuel chemical energy. Unfortunately, this quantity, the indicated efficiency, cannot be related analytically to fuel properties. It depends on an integration of the effects of fuel properties, engine design, and operating conditions as well as the ambient conditions at the inlet to the cylinder.

Based on the conventional fuel/air-cycle approximations a computer program for indicated efficiency was written, but it has not yet been run at the time of writing. So in making illustrative calculations of other operating parameters, indicated efficiency values from the literature were used in conjunction with one point calculated "by hand".

Some consideration is given to the calculations of the oxides of nitrogen generated by the combustion of H_2 and gasoline in piston engines. Simple models permit calculation of gross trends, but the results from more realistic models have not been reported for H_2. Nevertheless, it is possible to rationalize the published results of engine experience on a qualitative basis.

C.2.1 - Engine Thermodynamic Parameters

C.2.1.1 - Thermal Efficiency

The fraction of chemical energy input (Q_c) that appears as mechanical work output (W) is defined as the thermal efficiency (η). That is,

$$\eta \equiv \frac{W}{Q_c} \qquad (1)$$

For piston engines, if W represents work on the piston, then η is the indicated thermal efficiency. The efficiency is an extremely complex function of fuel properties, the engine itself, mixture fuel-to-air ratio fed to the engine, means of fuel introduction, cylinder inlet conditions, operating conditions, etc. Thus, many quantities must be exactly specified before W or η obtained from experiment can be rationally analyzed. Further consideration of η will be postponed until Section C.2.3.

The chemical energy input can be expressed as the product of an intrinsic fuel property, its chemical energy per unit mass (e_c) and the mass of fuel introduced (ω_F) so that Eq. 1 can be rewritten as

$$\frac{W}{\omega_F} = e_c \eta \qquad (2)$$

It is seen immediately that the chemical energy and efficiency have equivalent importance in producing a specific work output. Therefore, both must be examined when comparing fuels.

C.2.1.2 - Specific Fuel Consumption

The reciprocal of Eq. 2

$$\frac{\omega_F}{W} = \frac{1}{e_c \eta} \qquad (3)$$

is defined as the specific fuel consumption (SFC) and is a performance parameter commonly employed to characterize engine fuel economy. Since power output ($\mathcal{P}$) is the rate at which work is being done as a result of fuel flowing into the engine at the rate ($\dot{\omega}_F$), Eq. 3 can be rewritten as

$$SFC = \frac{\dot{\omega}_F}{\mathcal{P}} = \frac{1}{e_c \eta} \qquad (4)$$

which again shows explicitly the importance of e_c and η. For piston engines, if W is the work on the piston, then $\mathcal{P}$ is the indicated power.

C.2.1.3 - Power Output, Work Output and Mean Effective Pressure

The power output of air-breathing engines is limited by their ability to ingest air for oxidation of the fuel supplied. To reflect this, Eq. 4 is rearranged, and the air flow rate ($\dot{\omega}_A$) is introduced into numerator and denominator to yield

$$\mathcal{P} = \dot{\omega}_A \left(\frac{\dot{\omega}_F}{\dot{\omega}_A}\right) e_c \eta \qquad (5)$$

The term ($\dot{\omega}_F/\dot{\omega}_A$) is the fuel-to-air ratio of the mixture actually introduced into the engine. For every fuel there is a unique value of this ratio that produces, ideally, as combustion products only H_2O and N_2 when H_2 is burned, and only CO_2, H_2O and N_2 when hydrocarbons are burned. It is commonly referred to as the "stoichiometrically correct" ratio, $(F/A)_{st}$. Dividing or "normalizing" $\dot{\omega}_F/\dot{\omega}_A$ with this ratio yields the equivalence ratio (Φ) which is an index of fuel content, or "strength" or "quality" of the actual mixture introduced into the engine. Equation 5 then can be rewritten as

$$\mathcal{P} = \Phi \, \dot{\omega}_A \left(\frac{F}{A}\right)_{st} e_c \eta \qquad (6)$$

In particular, for positive displacement engines, the cyclic nature of their operation makes it convenient to consider $\dot{\omega}_A$ as the product of the mass of air that goes through the cycle, (ω_A/cycle), and the number of cycles per unit time that the engine undergoes. The work per cycle, W/cycle, through Eq. 2 can be related to ω_A/cycle, as

$$W/cycle = \Phi \left(\omega_A/cycle\right)\left(\frac{F}{A}\right)_{st} e_c \eta \tag{7}$$

And if Eq. 7 is multiplied through by the cycle rate, Eq. 6 is obtained.

Still another useful performance parameter of positive displacement engines is the amount of work done per cycle divided by the engine displacement (D). It is defined as the mean effective pressure (MEP), and is proportional to the engine torque (indicated). From Eq. 7:

$$MEP \equiv \frac{W/cycle}{D} = \Phi \frac{\left(\omega_A/cycle\right)}{D}\left(\frac{F}{A}\right)_{st} e_c \eta \tag{8}$$

Assuming that there is uniform distribution of charge throughout each element of each cylinder, MEP is an indication of how hard each element of every cylinder is working, and thus is a very useful engine parameter in the study of the influence of fuel properties on engine performance.

Note that (in contrast to SFC) $\mathcal{P}$, W/cycle and MEP depend <u>explicitly</u> on an additional intrinsic fuel property $(F/A)_{st}$, and an operating parameter, Φ, as well as the engine's capacity for air ingestion, $\dot{\omega}_A$, (ω_A/cycle) or $\left(\frac{\omega_A/cycle}{D}\right)$, respectively.

C.2.1.4 - Techniques for Controlling Engine Power Output

Inspection of Eq. 6 shows that control of $\mathcal{P}$ is possible by variation of $\dot{\omega}_A$ or Φ, since η is a function of both of these quantities, among others, and e_c and $(F/A)_{st}$ are intrinsic fuel properties.

Control of $\mathcal{P}$ through variation of $\dot{\omega}_A$ is referred to as "quantity control". It is used almost universally in carbureted, spark-ignition piston engines fueled with hydrocarbons. Generally, a decrease in power is achieved through the closure of a throttle valve to constrict the passage of air from the environment to the cylinder intake valve port.

When fueled with gasoline, for example, such engines exhibit a fuel-lean operation limit near $\bar{\Phi} = 0.75$ (Ref.12). And η decreases sharply with increasing $\bar{\Phi}$ above $\bar{\Phi} \approx 1.1$. This range of $\bar{\Phi}$ variation has been found to be too small for the quality control of their power.

However, when fueled with H_2, such engines can be operated down to $\bar{\Phi} \cong 0.15$ -- although η decreases sharply with decreasing $\bar{\Phi}$ below $\bar{\Phi} \cong 0.25$ (Ref.13). Thus, carbureted spark-ignition piston engines are susceptible to practical quality control when fueled with H_2, as recognized more than 50 years ago by Ricardo (Ref.14).

This is a prime example of how substitution of H_2 for a hydrocarbon fuel opens new possibilities for the control of a particular type of engine. Notice however, that this possibility is not new for other types of engines. Hydrocarbon fuels are currently employed in all operational gas turbine and diesel engines -- and their power output is varied by quality control.

By inspection of Eqs. 7 and 8, it is clear that W/cycle or MEP could be used equally well as a basis for discussion of quantity-vs quality control of engine output.

Since η is a different function of $\bar{\Phi}$, then it is of $\dot{\omega}_A$ (or ω_A/cycle or $\left(\frac{\omega_A/\text{cycle}}{D}\right)$ and since power depends on η, engine operations with these two different kinds of power control are not simply comparable even when the same fuel is used. If a different fuel is used with each kind, the fundamental influence of fuel properties on engine performance becomes even more difficult to discern by comparing the results.

C.2.1.5 - Positive-Displacement-Engine Air Capacity and "Volumetric Efficiency"

"Air capacity" is defined as the quantity of air an engine ingests per unit time. It is very important in positive-displacement engines since their power output is limited by their ability to ingest air in order to oxidize the fuel available.

During actual engine operation, air does not fill the entire displacement volume of the cylinders due to the presence of combustion product gases remaining from the previous cycle, moisture of the air ingested, and the fuel itself if it is introduced before closure of the inlet valve -- which, in the case of H_2, could occupy a significant fraction of the total displacement volume of the engine.

The rate at which displacement volume can be filled is equal to the cylinder displacement volume times the number of suction strokes by the engine per unit time. In a four-stroke engine there is one suction stroke per cycle for each cylinder, but the shaft must turn two revolutions to complete a cycle. Thus, for each cylinder, the number of suction strokes per unit time is equal to half the revolutions per unit time (N). So for a four-stroke engine with a total displacement of D, the rate at which volume is made available to the air is $ND/2$.

Multiplying this by the actual density of air in the cylinder at the time of inlet valve closure, ($\rho_{A,1}$) yields the actual engine air capacity, $(\dot{\omega}_A)_{actual}$, or

$$(\dot{\omega}_A)_{actual} \equiv \frac{ND}{2}\rho_{A,1} \tag{9}$$

Assuming that the chemical species that occupy the cylinder are all in the gaseous state, are uniformly distributed and obey the Ideal-Gas-Law equation-of-state, then,

$$\rho_{A,1} \equiv \frac{\omega_A/cycle}{D} = \frac{\overline{MW}_A \frac{\omega_A/cycle}{\overline{MW}_A}}{D} = \frac{\overline{MW}_A(n_A/cycle)}{D} = \frac{\overline{MW}_A P}{R T_1}\left(\frac{n_A}{n_T}\right)_{cycle} \tag{10}$$

where: P_1 is the pressure of the mixture

T_1 is the temperature of the mixture

η_A/cycle is the number of moles of air ingested per cycle

η_T/cycle is the total number of moles that occupy D per cycle

$\overline{MW_A}$ is the molecular weight of air

R is the Universal Gas Constant.

Thus

$$\rho_{A,1} = \frac{\omega_A/cycle}{D} = \frac{\overline{MW_A}\, P_1}{RT_1} \frac{1}{1 + \frac{\overline{MW_A}}{\overline{MW_F}}\left(\frac{F}{A}\right)_{st}\Phi + \frac{\overline{MW_A}}{\overline{MW_e}}\frac{\omega_e}{\omega_A/cycle} + \frac{\overline{MW_A}}{\overline{MW_M}}\frac{\omega_M}{\omega_A/cycle}} \quad (11)$$

where: $\overline{MW_F}$ is the fuel molecular weight

$\overline{MW_e}$ is the molecular weight of the residual combustion product per cycle

ω_e is the mass weight of the residual combustion product per cycle

ω_M is the mass moisture induced with the air per cycle

$\overline{MW_M}$ is the molecular weight of water

It is clear that T_1 is greater than the temperature of the engine inlet due to heat transfer to the fresh charge from hot engine parts and the effects of mixing with the hot residual combustion products. Also, P_1 is less than the pressure at the inlet due to dissipation associated with the intake process.

The "ideal air capacity" is the engine air capacity under ideal conditions. In the ideal, air taken from the environment would flow into the displacement volume, which contained no remaining combustion products, and reach the same temperature and pressure as that which existed at the inlet. It is sometimes useful to separate out the effect of moisture and fuel dilution of the air from the effects of the induction process and the presence of the combustion product gases remaining from the previous cycle. In such cases and in the present approach, the "ideal" is defined not as above, but in terms of the fuel-air mixture filling the displacement volume at the temperature and pressure at the inlet.

The "volumetric efficiency" (ϵ) is defined as the ratio of the actual air capacity to the ideal air capacity. This is not the usual sense of the word efficiency, and in fact it is really the ratio of the actual density of air in the displacement volume to the density of the air in the cylinder under ideal conditions.

Based on the ideal of induced fuel-air mixture filling the chamber at the pressure (P_i) and temperature (T_i) that exists at the engine inlet, the density of air in the mixture at the inlet condition, $\rho_{A,i}$ is

$$\rho_{A,i} = \frac{\overline{MW}_A P_i}{R T_i} \frac{1}{1 + \frac{\overline{MW}_A}{\overline{MW}_F}\left(\frac{F}{A}\right)_{st}\Phi + \frac{\overline{MW}_A}{\overline{MW}_M}\frac{\omega_M}{\omega_A/cycle}} \tag{12}$$

and, therefore, from Eq. 11 and Eq. 12:

$$\epsilon \equiv \frac{\dot{\omega}_A}{(\dot{\omega}_A)_{ideal}} = \frac{\left(\frac{ND}{2}\right)\rho_{A,1}}{\left(\frac{ND}{2}\right)\rho_{A,i}} = \frac{\omega_A/cycle}{(\omega_A/cycle)_{ideal}} = \frac{\frac{\omega_A/cycle}{D}}{\frac{(\omega_A/cycle)_{ideal}}{D}} \tag{13}$$

Substitution of the appropriate forms of Eq.12 and 13 into Eqs. 6,7 and 8 yields

$$P = \epsilon \frac{ND}{2} \frac{\overline{MW}_A P_i}{R T_i}\left[\frac{1}{1 + \frac{\overline{MW}_A}{\overline{MW}_F}\left(\frac{F}{A}\right)_{st}\Phi + \frac{\overline{MW}_A}{\overline{MW}_M}\frac{\omega_M}{\omega_A/cycle}}\right]\Phi\left(\frac{F}{A}\right)_{st} e_c \eta \tag{14}$$

$$W/cycle = \epsilon D \frac{\overline{MW}_A P_i}{R T_i}\left[\frac{1}{1 + \cdots\cdots}\right]\Phi\left(\frac{F}{A}\right)_{st} e_c \eta \tag{15}$$

$$MEP = \epsilon \frac{\overline{MW}_A P_i}{R T_i}\left[\frac{1}{1 + \cdots\cdots}\right]\Phi\left(\frac{F}{A}\right)_{st} e_c \eta \tag{16}$$

It is noted that still another intrinsic fuel property, $\overline{MW}_F$, influences positive-displacement engine performance when the fuel is introduced <u>before</u> closure of the inlet valve. The term in the brackets in which $\overline{MW}_F$ appears reflects the fact that a portion of D is occupied by fuel vapors. For H_2-fueled piston engines, the performance decrement due to this factor could be significant under certain conditions. For gasoline-fueled piston engines the maximum performance decrement due to this factor is only about 2%.

About 50 years ago, Erren (Ref.15) demonstrated experimentally that this $\overline{MW}_F$-related performance decrement could be eliminated simply by injecting the fuel directly into the cylinder <u>after</u> closure of the inlet valve. This will be referred to as CFI (for <u>c</u>ylinder <u>f</u>uel <u>i</u>njection after closure of the inlet valve). For CFI operation there is no fuel vapor in $\dot{D}$, so the term containing $\overline{MW}_F$ does not appear in Eqs. 14, 15 and 16.

In contrast to non-CFI operation (e.g., normal carburetor, inlet-manifold fuel introduction, fuel introduction at the inlet valve before valve closure, etc.), CFI operation involves "supercharging" the cylinders in that they contain a greater mass of mixture than would be ingested during non-CFI operation. Further, the engine cycle must be different since some of the mixture is pumped into the cylinder at a pressure greater than P_1, and the pump work must be taken into account in calculation of net work output and cycle efficiency. Thus, the performance of CFI engines and non-CFI engines are not simply comparable.

<u>C.2.2. - Illustrative Calculations</u>

In this section the influence of fuel properties on positive-displacement engine performance parameters are shown by means of illustrative calculations. The properties of H_2 and gasoline are used in the calculation of SFC (Eq. 4) and MEP (Eq. 16).

The influence of $\overline{MW}_F$ on the performance of non CFI engines is shown explicitly by Eqs. 14, 15 and 16. The influence of $\overline{MW}_F$ on the performance of CFI engines is felt through the amount of work required to pump the fuel into the cylinder and thus impinges on η --so it cannot be shown explicitly.

For expediency, the influence of $\overline{MW}_F$ on the performance of CFI engines will be ignored in making the illustrative calculations in this section. To signify that this has been done, the engine will be designated as "quasi-CFI".

C.2.2.1 - Assumptions

It will be assumed that η for both quasi-CFI and non CFI engine operation are the same at the same CR and Φ. This means that the influence of pumping work is ignored and that the engine cycles are equivalent. In fact, the only CFI feature accounted for here is the nonappearance of the $\overline{MW}_F$ term in Eq. 16.

Comparisons of SFC and MEP are made at values of Φ that have been found experimentally to result in maximum power and maximum efficiency. For H_2, these occur at $\Phi \cong 1.0$ and $\Phi \cong 0.45$, respectively (Ref. 16). And for gasoline they occur at $\Phi \cong 1.1$ and $\Phi = 0.85$, respectively (Ref. 12).

Values of η calculated for CR = 10/1 on the basis of the fuel/air-cycle approximation (see Section C.2.3.2) and displayed in Fig. C.3-3 are used. For H_2, $\eta = 0.44$ at $\Phi = 1.0$ and $\eta = 0.5$ at $\Phi = 0.45$. For gasoline, $\eta = 0.42$ at $\Phi = 1.1$ and $\eta = 0.48$ at $\Phi = 0.85$.

Further, it will be assumed that $\epsilon = 1$, that $\omega_M = 0$ and that both fuels are completely vaporized in the CFI mode of operation.

The properties of gasoline will be taken to be those of iso-octane, so that the following fuel properties apply.

Fuel	e_c^*	$(F/A)_{st}$	$e_c(F/A)_{st}$	$\overline{MW}_F$	$\frac{\overline{MW}_A}{\overline{MW}_F}(F/A)_{st}$
H_2	51,600	0.029	1,500	2	0.42
Iso-octane	19,100	0.067	1,280	114	0.017

TABLE C.2-1: Fuel Properties for Hydrogen and Iso-Octane (Ref 17)

C.2.2.2 - Results

Insertion of the appropriate values into Eq. 4 and Eq.16 yields

Engine Performance	MAXIMUM POWER $\Phi_{H_2} = 1.0$; $\eta_{H_2} = 0.44$ $\Phi_{iso} = 1.1$; $\eta_{iso} = 0.42$		MAXIMUM EFFICIENCY $\Phi_{H_2} = 0.45$; $\eta_{H_2} = 0.5$ $\Phi_{iso} = 0.85$; $\eta_{iso} = 0.48$	
	non-CFI	quasi-CFI	non-CFI	quasi-CFI
$\frac{SFC_{H_2}}{SFC_{iso}}$	← 0.35 →			
$\frac{MEP_{H_2}}{MEP_{iso}}$	0.80	1.11	0.55	0.65

TABLE C 2.-2: Comparison of H_2 and Iso-Octane Performance of Positive-Displacement Engines for quasi-CFI and non CFI Operation (CR=10/1)

* The lower heat of combustion is used here for e_c.

SFC comparisons show that H_2 is better than iso-octane by a factor of about 2.8 at the point of maximum power output. And when Φ is adjusted for each to give maximum efficiency, H_2 is superior to iso-octane by about the same amount.

MEP comparisons show the importance of fuel-introduction technique. At maximum power, if CFI is not used, the loss in air capacity reduces the MEP for H_2 operation by about 20% below the MEP obtained with iso-octane. While if CFI is used, the MEP for H_2 will be about 11% greater than that obtained with iso-octane.

When compared at the respective conditions for maximum η, the relatively low Φ required for H_2 operation compared to that for iso-octane (i.e., 0.45 vis-a-vis 0.85) results in a severe drop of the MEP for H_2 compared to the MEP for iso-octane. For CFI operation, the MEP is only 65% of that obtained with iso-octane and for non-CFI operation it falls even further, to 55%. Assuming the engines were operating at the same speed, had the same number of cylinders and the same displacement, then the power penalty would be the same as the MEP penalty, as shown by Eq. 14 and Eq. 16.

As discussed in Section C.2.1.5, if the same engine is operated with H_2 and iso-octane at the same value of Φ, then the emission of the oxides of nitrogen (NO_x) air pollutants should be about the same. However, the emission of this pollutant is so sensitive to Φ, that at the maximum efficiency values for both fuels, the emission of NO_x with H_2 falls to somewhere between a hundredth to a thousandth of that with iso-octane.

Thus, in order to receive the maximum benefit in fuel economy and the benefit of greatly reduced NO_x emission, operation of H_2-fueled engines near $\Phi = 0.45$ is called for. However, the accompanying power penalty, relative to iso-octane best-economy operation of the same engine, must be taken. Naturally, this power penalty could be compensated for by increasing engine speed and/or size, or perhaps, by "supercharging" to increase P_1, or using cryogenic H_2 to reduce T_1. However, these speculations relate to the system within which the engines will work, and such considerations are beyond the scope of this present

document.

An example of the extent to which quality control (i.e., Φ variation) of H_2-engine MEP might be used can be calculated by means of Eq. 16. The data in Fig. C.3-3 show that for H_2 at $\Phi = 1$, $\eta = 0.44$ and at $\Phi = 0.45$, $\eta = 0.5$, when placed into Eq.16 yield

$$\frac{MEP_{H_2} @ \Phi = 0.45}{MEP_{H_2} @ \Phi = 1.0} \simeq 0.51$$

for quasi-CFI engines, and:

$$\frac{MEP_{H_2} @ \Phi = 0.45}{MEP_{H_2} @ \Phi = 1.0} = 0.61$$

for non-CFI engines. The experimental data of Fig.C.3-2 agree Φ data for H_2 as shown in Fig. C.3-2.

C.2.3 - Calculation of Indicated Efficiency

The indicated efficiency of an engine depends on many factors, including fuel type, Φ, state of the mixture at the engine inlet, thermodynamic cycle (i.e., sequence of states of the mixture and its combustion products), combustion time, heat transfer losses, etc. The totality of factors involved is so large and their interactions so complex that it is impossible to model them exactly in detail as a basis for calculation.

Historically, in lieu of an exact model, a succession of simplistic models of increasing realism have been used as a basis for calculation.

Naturally, hydrocarbon-air mixtures have been the subject of such modeling and calculations for many years. Only recently have H_2 -air mixtures been modeled, and then for only a limited range of variables in the more simplistic models (Ref 18). One objective of the subject program is to advance the calculations for H_2-air mixtures.

Almost all of the H_2-fueled positive-displacement engine data acquired to date have been obtained with engines nominally operating on the Otto cycle. This cycle is, therefore, of most interest here.

C.2.3.1 - The Air-Standard-Cycle Approximation

The air-standard-cycle approximation for engines involves two classes of approximations: One has to do with idealization of the working fluid that goes through the cycle and the other has to do with idealization of the cycle itself.

The working fluid, that is, the fuel-air mixture and its combustion products, are assumed to have constant specific heats, and have the same physical constants (e.g., molecular weight) as air.

The ideal Otto cycle involves consideration of a fixed working fluid that goes through a succession of thermodynamic states from the initial state at T_1 and P_1 (with the piston at bottom dead center) to return the fluid to its initial state.

This approximation results in a simple equation relating η to: (i) engine compression ratio (CR) and (ii) the ratio of the specific heat of the working fluid at constant pressure to its specific heat at constant volume (k),

$$\eta = 1 - \left(\frac{1}{CR}\right)^{k-1} \qquad (17)$$

In practice, all of the assumptions are violated, and the values of η found experimentally fall far short of those predicted by Eq. 17.

C.2.3.2 - The Fuel/Air-Cycle Approximation

This level of approximation is based on the real properties of the intake mixture and combustion-product gases in the idealized Otto cycle described in C.2.3.1. The level of complexity introduced is such that η can no longer be explicitly related to CR or any other variable. Numerical computations of η can be made, however. The technical literature contains many examples typified by those of Ref. 19 for hydrocarbon-air mixtures.

For H_2-air mixtures, a search of the literature revealed only one publication reporting the results of calculations of η for the fuel/air-cycle approximation (Ref. 18). They were made for $\Phi = 0.365$ and $\Phi = 0.48$ and are presented graphically in Fig.C.3-3.

Also plotted is one point at $\Phi = 1$ calculated by hand during the subject program. They are consistent with the expectation that η should decrease as Φ increases. An increasing fraction of the chemical energy of the working fluid becomes unavailable for useful work because of dissociation of the combustion products and because of increases in the specific heats of these products. And eventually, for $\Phi > 1$, η should fall sharply with further increase of Φ due to expulsion of unburned fuel in the exhaust (due to lack of oxygen in the mixture).

A computer program has been written with the intention of calculating η over a broad range of variation of Φ and CR and other performance parameters. The calculations had not been completed at the time this document was written. Therefore, fundamental comparisons of H_2 with hydrocarbon fuels on the basis of fuel/air-cycle approximations can be made only on a very limited basis at this time.

C.2.4 - Air Pollution Considerations

Carbon monoxide, unburned hydrocarbons, and the oxides of nitrogen (NO_x) are generated during the operation of hydrocarbon-fueled engines. Hydrogen-fueled engines generate only NO_x due to the absence of carbon atoms -- assuming, of course, carbon-containing lubricants do not inadvertently enter the cylinder and burn. Thus, H_2 is inherently superior to hydrocarbons in this regard. The remainder of this section will deal with NO_x generation and emission associated with H_2-fueled engines.

C.2.4.1 - NO_x Calculations Based on the Fuel/Air-Cycle Approximation

Within the framework of the fuel/air-cycle approximation (Section C.2.3.2), the NO_x concentration at the maximum cycle temperature can be readily calculated as a result of the thermodynamic and chemical equilibrium that is assumed to exist in the combustion products.

Such calculations have been performed by others (Ref. 20) over a rather limited range of variation (i.e., between 0.8 and 1.2) for standard conditions at the inlet of an engine operating at CR = 9. Apparently, these are the only results of NO_x

calculations for H_2-fueled, Otto-cycle engines that appear in the open literature. They are displayed in Fig. C.3-5, and along with the results for gasoline, are also shown in Figure C.3-7. These calculations indicate that both fuels will result in about the same concentration of NO_x at the same value of ϕ, with H_2 combustion generating slightly greater concentrations.

An indication of the calculated dependence of NO_x concentration on ϕ, when ϕ is decreased below 0.8 can be found in Ref. 21. These calculations were carried out for jet propulsion fuel and H_2 burned at constant pressure of 5 atmospheres, in a gas-turbine combustor that has a mixture inlet temperature of $800^{o}K$. Therefore, they cannot be compared quantitatively with the calculated results of Ref.20, but they do have several useful aspects; First, they show that as ϕ is reduced below 0.8 or so the NO_x concentration reaches a maximum and then falls again; Second, comparative values for aviation fuels are presented; Third, and perhaps most importantly, a separate set of calculations have been made by the authors which account for the rate of generation of NO_x in the combustion products, i.e., the concentration of NO_x in the combustion products is calculated at a time of two milliseconds after burning (as well as at equilibrium) --and this chemical kinetic calculation is an extension beyond usual fuel/air-cycle approximation calculations.

All of the calculated results that appear in Ref.20 and Ref. 21 show that H_2 is expected to generate a bit more NO_x than practical hydrocarbon fuels at the same value of ϕ. So, on this basis, H_2 is slightly inferior to hydrocarbon engine fuels.

C.2.4.2 - Reduction of No_x by Operation at Low ϕ

It has been found that naturally-aspirated, reciprocating engines, when H_2-fueled exhibit a much lower lean limit of operation (lower ϕ) than when they are operated with hydrocarbons (Section C.3). And it is this ability to operate at low ϕ (say, $\phi \leq 0.5$) that yields for H_2 the benefit of low NO_x production. However, as shown in Section C.2.2.2, for H_2-fueled positive-displacement engines, the MEP at $\phi = 0.45$ compared to that at $\phi = 1.0$ is calculated to be lower by .51% for quasi-CFI operation and 0.61 for non CFI operation. So a power penalty cannot be avoided at low .

C.2.4.3 - Calculations of NO_x Emissions from Engines

The fuel/air-cycle approximations are sufficiently removed from the reality of actual engine operation that calculations of NO_x concentration based upon it are not expected to correspond to NO_x concentrations found in the exhaust of operating engines. The authors of Ref. 22 have constructed a model that accounts for NO_x-concentration non-uniformities throughout the cylinder resulting from combustion initiation before piston top-dead-center, heat losses to the walls and finite rate of combustion wave travel. These influences can be coupled with a kinetic model for the finite rate of formation of NO_x in the combustion-product gases as well as finite rate of decomposition in the combustion products as they are cooled by expansion during the power stroke. This permits calculation of the NO_x concentration in the exhaust gases leaving the engine. Only the results with hydrocarbon fuels have been published, though reportedly (Ref. 28), calculations are in process for the case of H_2-fueled engines.

Comparison of experimental results with NO_x emissions calculated by this more complex model permits rationalization of the influence of engine operating conditions other than Φ and inlet conditions, e.g., engine speed and degree of spark-advance. For example, retarding the degree of spark advance generally results in a decrease in NO_x emissions. The faster burning velocity of H_2-air mixtures relative to gasoline-air mixtures frequently leads to H_2-fueled engines being operated with a degree of spark advance that is relatively retarded compared to hydrocarbon-fueled engines. Based on this consideration, the NO_x emissions from H_2-fueled engines would be expected to be lower than that from hydrocarbon fueled engines. However, other factors are important as well.

Until these more complex models are reality-tested, and more calculations are performed for the case of H_2-fueled operation, more detailed comparison of NO_x emissions are not warranted. However, quantitatively, at the same value of Φ, the slightly larger concentrations of NO_x generated by H_2-fueled operation (Fig.   ) will tend to be reduced by spark-retardation, etc. so that the NO_x actually emitted in the engine exhaust   be about about the same for H_2 and gasoline operation.

C.2.5 - References

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C.3 - RECIPROCATING ENGINES: SUMMARY & EVALUATION OF OPERATING EXPERIENCE

C.3.1 - Introduction

The widespread current use of reciprocating engines, both mobile and stationary, warrants attention as a potential application for hydrogen fuel. The "recip" has been developed extensively into a low cost, reliable powerplant, competitive in power and efficiency with other hydrocarbon-fueled engines. While not nearly so developed as its gasoline-fueled counterpart, the hydrogen-fueled recip has already shown enough promise so as to be the most-investigated of hydrogen-fueled powerplants.

Owing to its similar thermodynamics and application, the "rotary combustion" (Wankel) engine is treated in this section along with other types of true reciprocating engines. Each of these categories has been investigated experimentally, but most attention has been given to the hydrogen/air, spark-ignition engine.

Operating experiences with hydrogen-fueled reciprocating engines can be readily categorized by way of the reactants used:

(i) hydrogen/air
(ii) hydrogen + other fuel/air
(iii) hydrogen/oxygen

or by way of engine type:

(i) spark ignition
(ii) compression ignition

or by way of induction method:

(i) naturally-aspirated
(ii) supercharged

Reciprocating heat engines (e.g., Stirling and Feher-cycle engines) which do not use hydrogen combustion products as a working fluid are not dealt with in this section.

C.3.2 - Hydrogen/Air Engines

C.3.2.1 - Background

As mentioned above, the spark-ignition hydrogen/air engine has been most widely investigated, in fact, since the 1920's. Compression-ignition hydrogen engines were used in the 1920's and 1930's but no operating experience appears to have been reported since World War II.

Until about 1970, published data on hydrogen operation of reciprocating engines has been almost exclusively from single-cylinder, naturally-aspirated,(non-CFI),test-bed engines. While some early multi-cylinder operating experience is recognized, quantitative data and operational details are very incomplete. Similarly, reports of fuel-injection at either low or high pressure has been very limited. Expectedly, it did not prove difficult for engines designed primarily for gasoline to be operated on hydrogen, as anticipated even by an early science-fiction writer (see Ref. 1). No major accidents have occurred during such operations, though a few engine failures attributable to hydrogen use have been reported e.g., (Ref. 2).

The major operational problem exposed to date is that of performance. As is shown below, all available quantitative test data indicate, for example, a substantial decrease in peak power available from a naturally aspirated spark-ignition engine operated with hydrogen rather than gasoline. This is consistent with the fundamental considerations and illustrative calculations of Section C.2, above. In contrast, however, spark-ignition supercharged (including CFI) engines and compression-ignition engines have not been investigated enough to allow such statements.

The summaries following draw performance information from such operational data as are available. Performance variables such as:

(i) power output

(ii) specific power output (power/displacement, power/piston area)

(iii) mean effective pressure

(iv) thermal efficiency
(v) exhaust emissions

are emphasized in relation to operating variables such as:

(i) compression ratio
(ii) equivalence ratio (fuel/air mass ratio relative to stoichiometrically correct)
(iii) speed (of rotation and of piston displacement)

As is seen below, a comprehensive view of prior experimental data of this type allows a useful quantitative characterization of hydrogen-fuel operations, at least for the naturally-aspirated spark-ignition engine.

C.3.2.2 - Spark-Ignition Engines - Overall

The historical trend of experience with hydrogen-fueled spark-ignition engines is apparent in Tables C.3-1 and C.3-2. These tables of engine specifications summarize prior conditions for operating both unmodified "Otto-cycle" engines and those recent engines which have been "modified" to provide for exhaust-gas recirculation ("EGR") and water-injection ("WI"). "Quality control" (fuel/air ratio variation), rather than "quantity control" (throttling), has been used with rare exception. It is noteworthy that virtually all these engines have been used for relatively modest test programs using hydrogen as a fuel. Often very specific reasons for testing limit the data obtained, e.g., the knock-limit tests of Downs et al. (Ref. 3) or Anzilotti et al. (Ref. 4,5). In other cases, testing was for demonstration purposes, e.g., for the 1972 Urban Vehicle Design Contest (Ref's. 6, 7). More recently, specific concerns for part-load efficiency (Ref. 8) and pollutant emissions (Ref. 9,10) have yielded data that are interesting new explorations. However, again, these are compromised in utility owing to the limited test aims, programs, (and presumably funding) involved. Several current investigations are reportedly of somewhat more comprehensive scope (Ref's. 11,12), but data have not yet been reported from these. Typical of presently-available data is a lack of indicated (rather than the less-useful brake) horsepower data at commonly high piston speeds over

TABLE C.3-1: SUMMARY OF HYDROGEN/AIR ENGINE EXPERIENCE - ENGINE SPECIFICATIONS & POWER OUTPUT

INVESTIGATOR	NO. OF CYLINDERS	DISPLACEMENT (IN^3)	COMPRESSION RATIO	MAX. ENGINE SPEED (RPM)	MAX. PISTON SPEED (FT/MIN)	MAX. REPORTED POWER (HP)	MAX. POWER / DISPLACEMENT (HP/IN^3)	MAX. POWER / PISTON AREA (HP/IN^2)
Tizard (Ref. 48)	1	127	-	-	-	-	-	-
Ricardo	1	127	5.45/1	1500	2000	28	.22	1.76
(Ref. 20)	"	"	7/1	"	"	36	.28	2.26
(Ref. 29)	1	127	5.45/1	1500	2000	-	-	-
Burstall (Ref. 21)	1	127	5/1	1000	1333	15.5	.12	0.97
	"	"	7/1	"	"	18.7	.15	1.18
Erren (Ref. 1)	-	-	8/1	-	-	-	-	-
Egerton (Ref. 47)	-	-	-	-	-	-	-	-
Oemichen (Ref. 27)	-	-	12/1	1500	-	-	-	-
King (Refs. 2,16, 22,23)	1	37	4/1-20/1	1800	1350	12	.32	1.44
Downs (Ref. 3)	1	31	8/1-20/1	1500	-	-	-	-
Anzilloti (Refs. 4,5)	1	37	8/1-12/1	900	625	-	-	-

TABLE C.3-1 (CONT'D.)

INVESTIGATOR	NO. OF CYLINDERS	DISPLACEMENT (IN^3)	COMPRESSION RATIO	MAX. ENGINE SPEED (RPM)	MAX. PISTON SPEED (FT/MIN)	MAX. REPORTED POWER (HP)	MAX. POWER / DISPLACEMENT (HP/IN^3)	MAX. POWER / PISTON AREA (HP/IN^2)
Holvenstot (Ref. 15)	8	3850	8/1	550	825	217	.056	.51
Karim (Ref. 25)	1	37	6/1-16/1	900	675	-	-	-
(Ref. 26)	1	37	14/1-20/1	900	675	-	-	-
Swain (Ref. 13)	4	98	9/1	2600	1200	16 (1)	.16 (1)	-
Billings (Ref. 9)	1	6.65	5.5/1	2900	725	1.64	.25	.370
Adt (Ref. 45)	4	197	10/1	1400	875	6.9 (1)	.035 (1)	.13 (1)
Finegold (Ref. 6)	8	351	8.9/1	-	-	-	-	-
Lynch (Ref. 24)	Various, few details given							
Adt (Ref. 46)	8	197	10/1	1450	906	16.8 (1)	.085 (1)	.33 (1)
Breshears (Ref. 43)	8	-	-	2000	-	-	-	-
Finegold (Ref. 8)	8	350	8.5/1	1500	870	43	.12 (1)	.43 (1)
Stebar (Ref. 10)	1	37	8/1	1200	900	1.3	.035	.16

TABLE C.3-1 (CONT'D.)

INVESTIGATOR	NO. OF CYLINDERS	DISPLACEMENT (IN^3)	COMPRESSION RATIO	MAX. ENGINE SPEED (RPM)	MAX. PISTON SPEED (FT/MIN)	MAX. REPORTED POWER (HP)	MAX. POWER / DISPLACEMENT (HP/IN^3)	MAX. POWER / PISTON AREA (HP/IN^2)
Thomas (Ref. 28)	4	140	8/1	2500	1500	12.$^{(1)}$	.086$^{(1)}$	.31$^{(1)}$

NOTES:
(1) based on brake rather than indicated horsepower

TABLE C.3-2: SUMMARY OF HYDROGEN ENGINE EXPERIENCE - PARTIAL PERFORMANCE DATA

INVESTIGATOR	AT MAX. REPORTED POWER				AT MAX. REPORTED EFFIC.				PERFORM-ANCE CURVES?
	EQUIV. RATIO, Φ	THERMAL EFFIC., η (%)	MEP (PSI)	EXHAUST NO_x (PPM)	EQUIV. RATIO, Φ	THERMAL EFFIC., η (%)	MEP (PSI)	EXHAUST NO_x (PPM)	
Tizard (Ref. 48)	-	-	-	-	-	-	-	-	-
Ricardo	sl.>1.0	31	115	-	.38	38	60	-	Yes
(Ref. 20)	-	43[3]	74[3]	-	-	-	-	-	No
(Ref. 29)	.9[4]	33[4]	-	-	.9[4]	40[4]	-	-	No
Burstall (Ref. 21)	.77 .85	31 37	94 118	-	.38 .50	35 38	53 77	-	Yes
Erren (Ref. 1)	-	45	-	"none observed"	-	45	-	"none observed"	No
Oemichen (Ref. 27)	-	-	-	-	-	52	-	-	No
King (Refs. 2,16, 22,23)	1.0	38 (CR = 14/1)	143	-	.39	52 (CR = 20/1)	60	-	Yes
Downs (Ref. 3)	-	-	-	-	-	-	-	-	No
Anzilloti (Refs. 4,5)	-	-	-	-	-	-	-	-	No

TABLE C.3-2 (CONT'D.)

INVESTIGATOR	AT MAX. REPORTED POWER				AT MAX. REPORTED EFFIC.				PERFORMANCE CURVES?
	EQUIV. RATIO, Φ	THERMAL EFFIC., η (%)	MEP (PSI)	EXHAUST NO_x (PPM)	EQUIV. RATIO, Φ	THERMAL EFFIC., η (%)	MEP (PSI)	EXHAUST NO_x (PPM)	
Holvenstot (Ref. 15)	≅1.0	29 (1)	82 (1)	-	-	-	-	-	Yes
Karim (Ref. 25)	-	-	-	-	-	-	-	-	No
(Ref. 26)	-	-	-	-	-	-	-	-	No
Swain (Ref. 13)	-	-	50 (1)	1900	-	-	-	-	No
Billings (Ref. 9)	.8-.9	33-23	66	7000	.5	34	53	2.5	Yes
Adt (Ref. 45)	.28	17 (1)	19 (1)	2.2	-	-	-	-	Yes
Finegold (Ref. 6)	-	-	-	-	-	-	-	-	No
Lynch (Ref. 24)	-	-	-	-	-	-	-	-	No
Adt (Ref. 46)	.47	25 (1)	47 (1)	-	.37	28 (1)	38 (1)	-	
Breshears (Ref. 43)	-	-	-	-	.35	39	-	.06 gm/ihp-hr	Yes
Finegold (Ref. 8)	≅.6	31 (1)(3)	65 (1)(3)	12	-	-	-	-	Yes
Stebar (Ref. 10)	.2 (2)	40 (2) (Lean-limit-operation)	23 (2)	13 (2) gm/ihp-hr	-	-	-	-	Yes

TABLE C.3-2 (CONT'D.)

INVESTIGATOR	AT MAX. REPORTED POWER				AT MAX. REPORTED EFFIC.				PERFORMANCE CURVES?
	EQUIV. RATIO, ϕ	THERMAL EFFIC., η (%)	MEP (PSI)	EXHAUST NO_x (PPM)	EQUIV. RATIO, Φ	THERMAL EFFIC., η (%)	MEP (PSI)	EXHAUST NO_x (PPM)	
Thomas (Ref. 28)	-	23 (1)(2)	27 (1)(2)	-	-	-	-	-	No

NOTES:
(1) based on brake rather than indicated horsepower
(2) not at maximum power; only one operating point reported
(3) limited by preignition and/or backfire
(4) varying % heat rejection reported at varying % full load

a range of speeds and fuel/air ratios.

Reported performance is summarized in Table C.3-1 and C.3-2 for "unmodified" and "modified" engines. Cases for which performance curves of any type are available are identified. However, it was judged sufficient in summarizing briefly to characterize just two key operating points, whenever possible:

(i) "maximum" power output ("P_{max}")
(ii) "maximum" thermal efficiency ("η_{max}")

In each case, the term "maximum" implies simply the conditions of the largest reported value for either performance variable; the values are not necessarily the maxima which might have been observed using a different or more complete test plan, etc.

C.3.2.3 - "Unmodified" Naturally-Aspirated Spark-Ignition Engines

In this section only those engine operations are considered which involve the admission of hydrogen and air together into the engine cylinder. "Port injection" (Ref.13) is counted in this class. Direct injection of fuel into the engine cylinder (CFI) is considered below under the separate heading of "supercharged" engines; the effects of such hydrogen injection hinder direct comparison between operation with natural aspiration and with injection.* Data from operations involving EGR and WI are considered in the next section.

Collected thermodynamic performance data are shown in Figs. C.3.1 and C.3-2 where thermal efficiencies (η) and mean effective pressures (MEP) are plotted as functions of equivalence ratio (Φ). The points shown represent values calculated from experimental data in a way which allows rough comparison despite

* While not explicitly recognized in Ref.14, direct injection of gaseous hydrogen into the (closed) cylinder in effect yields variable supercharging as equivalence ratio is varied. Though not highly significant in the case of high-molecular-weight hydrocarbon fuels, this effect is substantial with (low-molecular weight) hydrogen.

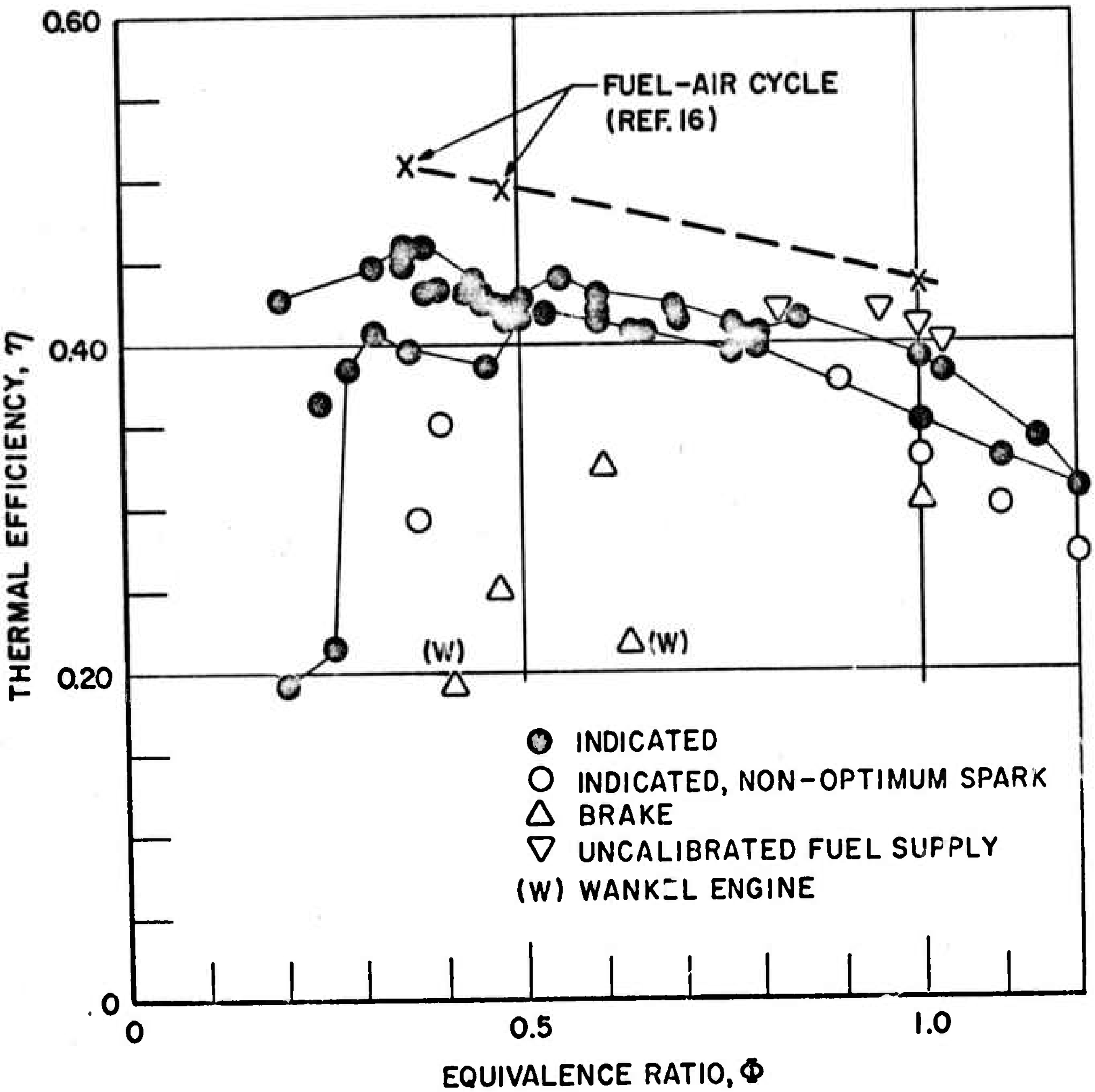

FIGURE C.3-1: Collected Experimental Thermal Efficiencies of H_2/Air, Non-CFI Engines (Data scaled to common CR = 10/1)

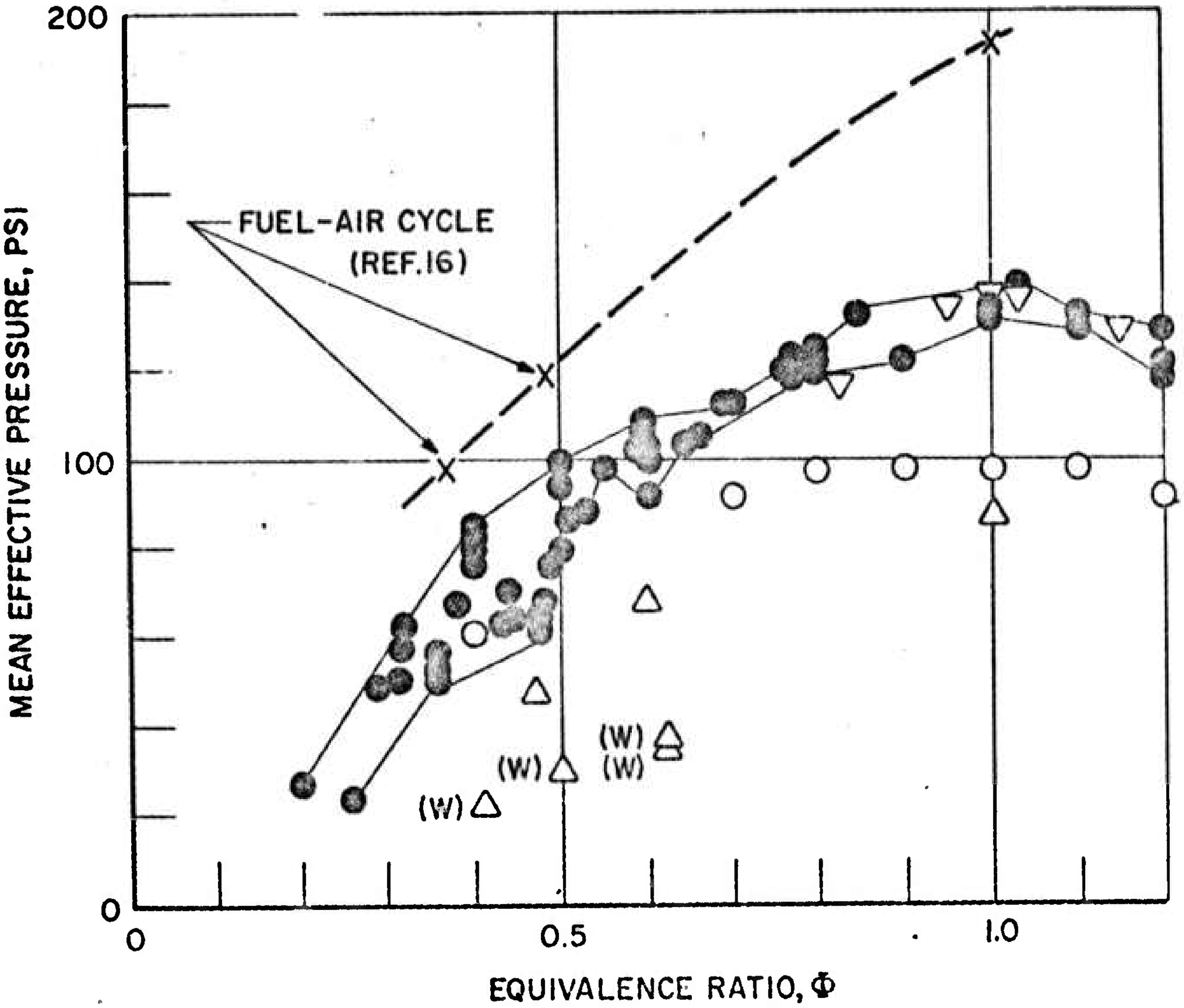

FIGURE C.3-2: Collected Experimental Mean Effective Pressures of H_2/Air, Non-CFI Engines (Data scaled to common CR = 10/1)

the differences in compression ratios at which the experimental data were obtained. The method used was that of scaling each reported efficiency to the corresponding efficiency at a common, reference CR (10/1) via:

$$\eta_{\text{SCALED TO CR}=10/1} = \eta_{\text{TEST CR}} \frac{(\eta_{\text{AIR STD}})_{\text{CR}=10/1}}{(\eta_{\text{AIR STD}})_{\text{TEST CR}}}$$

MEP data were similarly scaled, though the process is less justifiable in this case; there are CR influences on MEP from sources beyond those that influence efficiency (volumetric efficiency effects). One such is intake (manifold) pressure. Most of the hydrogen-engine data reported are apparently for wide-open throttle (WOT) operation. However, in two cases (Ref's 9,15), there is concrete evidence that manifold pressures were substantially below atmosphere. In one case (Ref. 9), the sub-atmospheric manifold pressure is cited, and the MEP data from this reference were corrected to standard-pressure intake conditions to allow direct comparison with other WOT data. The other data which could not be corrected in this manner are not included in Fig's. C.3-1 and C.3-2.

Experimental data for hydrogen injection directly into the cylinder (CFI) are not included (Ref.14).

In a few cases, only η-vs-Φ data were available experimentally. These efficiency data might have been extended into MEP-vs-Φ data using Eq. 16 and the assumption that volumetric efficiency is 100%.* However such MEP data are not strictly comparable with directly measured MEP values; the latter can be expected to be lower owing to actual volumetric efficiencies less than 100%. Therefore, only directly measured MEP's are displayed in Fig. C.3-2; none calculated from efficiencies have been included.

Shown for reference in Figs. C.3-1 and C.3-2 are several calculated values from fuel/air-cycle analysis of the hydrogen/air engine: indicated efficiencies are shown for Φ = 0.365 and 0.48

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* i.e., that there is no net effect of residual product gas and of density change of the intake mixture during induction.

(Ref. 16) and for $\Phi = 1.0$ (preliminary calculation from the present program). In one case ($\Phi = 1.0$), a corresponding directly calculated MEP value is available; however, in the others directly calculated MEP data are not available. Therefore, to produce three comparable fuel/air-cycle values for MEP to display in Fig. C.3-2, efficiency data were used to calculate all fuel/air cycle MEP values indirectly as described immediately above by assuming volumetric efficiency (ε) to be 100%.

Considering the wide variety of engines (and compression ratios) from which the data were obtained, some data scatter is to be expected but rough trends are clearly evident. The trends indicated by the experimental data are reasonable in comparison with the calculated values.

The experimental efficiencies are 80 to 90% of the calculated fuel/air cycle efficiencies for hydrogen/air. This 80 to 90% range in volumetric efficiency includes the 80 to 85% range expected in gasoline engines. However, the 90% extreme is high compared with gasoline/air values. It is notable that the highest efficiency values in comparison with fuel/air-cycle values come from the efforts of King (Ref. 16). While King worked carefully and more extensively than other investigators, there is still no assurance that his values represent the best attainable; he was, after all, working with engines only slightly modified from their original, gasoline-operation designs.

It has been proposed that some losses in the real hydrogen engine (e.g., combustion-time losses) might be lower than with gasoline. The highest of the values assembled here lend some substantiation to this proposal. However, further evaluation of this probability requires currently unavailable experimental data for both gasoline and hydrogen in the same engine (at the same Φ or over the same Φ range) and the comparison of these data with fuel/air-cycle calculations which have not presently been reported. The possibility of doing such a comparison is limited to the range for which gasoline can be burned ($\Phi > 0.75$), and the only current data for both gasoline and hydrogen operation in this range

(with the same engine) are those of Billings (Ref. 9). Unfortunately, Billings' data are not for optimum spark advance (e.g., max.Brake MEP). Therefore, Billings' data are not usable for judging the relative attainment of fuel/air-cycle performance by gasoline and hydrogen engines.

The experimental MEP data of Fig. C. 3-2 are more extensive (and also more scattered) than the hydrogen-engine efficiency data. The measured MEP values are 60 to 80% of those calculated from fuel/air cycle efficiencies. These actual MEP data can be expected to be lower than those shown in Fig. C.3-2 and those calculated from fuel/air-cycle efficiencies for two reasons:

(i) Actual ε less than calculated

(ii) $\varepsilon < 1$

As discussed above, the actual efficiencies are 80 to 90% less than those calculated. Therefore, the 60 to 80% factor between calculated MEP and actual MEP implies volumetric efficiency of 75 to 90% for $0.4 < \Phi < 1.0$. Such a volumetric-efficiency range is comparable with volumetric efficiencies of gasoline engines.

While volumetric efficiencies could be calculated from the actual efficiency and MEP data (see Eq. 16), this has not been done. The lack of reported intake conditions in most cases makes such calculations for individual cases questionable.

In summary, actual efficiencies of hydrogen engines appear to be approximately the same fraction or somewhat higher (80 to 90%) than the fraction of fuel/air-cycle efficiencies in gasoline engines. Actual volumetric efficiencies are comparable (approx. 75 to 90%) with gasoline and with hydrogen operation. This suggests that the relative performance of gasoline and hydrogen engines can reasonably be assessed from the relative performance indicated by fuel/air-cycle calculations for the two fuels. While such a conclusion is justified as regards gasoline, the correlation between actual and fuel/air-cycle performance has not been established previously; only over one narrow range of Φ (0.365 to 0.48) has this relationship been established previously for hydro-

gen engines and only for one particular engine (Ref. 16).

Recognizing the value of <u>fuel/air-cycle comparisons</u>, full fuel/air-cycle calculations for hydrogen engines are called for. These have been initiated as part of the present program, but calculations are presently incomplete. The limited calculated points currently available are, however, useful. By choice, they are in the neighborhood the the actual maximum-power and maximum-efficiency points for hydrogen engines (Φ = 1.0, Φ = 0.4 - 0.5; respectively). A comparison of fuel/air cycle efficiencies and MEP's at these points is called for.

Fig. C-3-3 shows fuel/air-cycle (indicated) efficiencies for gasoline (from Figs. 4-5, Ref. 17) and those already presented for hydrogen. At Φ = 1. i.e., approximately maximum power, calculated hydrogen-engine efficiency is approximately 95% that calculated for gasoline. At Φ = 0.48, i.e., approximately maximum efficiency, the hydrogen-engine value is also about 95% that for gasoline. While in each case the hydrogen values are lower, it must be recalled that actual carburetted gasoline engines will not operate below Φ= 0.75 and show actual peak efficiencies at, say, Φ = 0.85. A fair comparison of efficiencies at maximum efficiency operation would then involve Φ = 0.8 for gasoline and Φ = 0.45 for hydrogen. From the fuel/air-cycle calculations, then:

$$\frac{(\eta_{\Phi = 0.45})_{H_2}}{(\eta_{\Phi = 0.85})_{Gaso.}} = \frac{.500}{.475} = 1.05$$

Therefore, approximately 5 percent greater efficiency might be expected from a hydrogen engine as from a gasoline engine, each operating at its respective maximum-efficiency condition (with wide-open throttle, WOT), based on fuel/air-cycle calculations.

Fig. C.3-4 shows fuel/air cycle (indicated) mean effective pressures for gasoline and for hydrogen. At Φ= 0.5, directly calculated MEP values are not available (Ref.16), and, therefore,

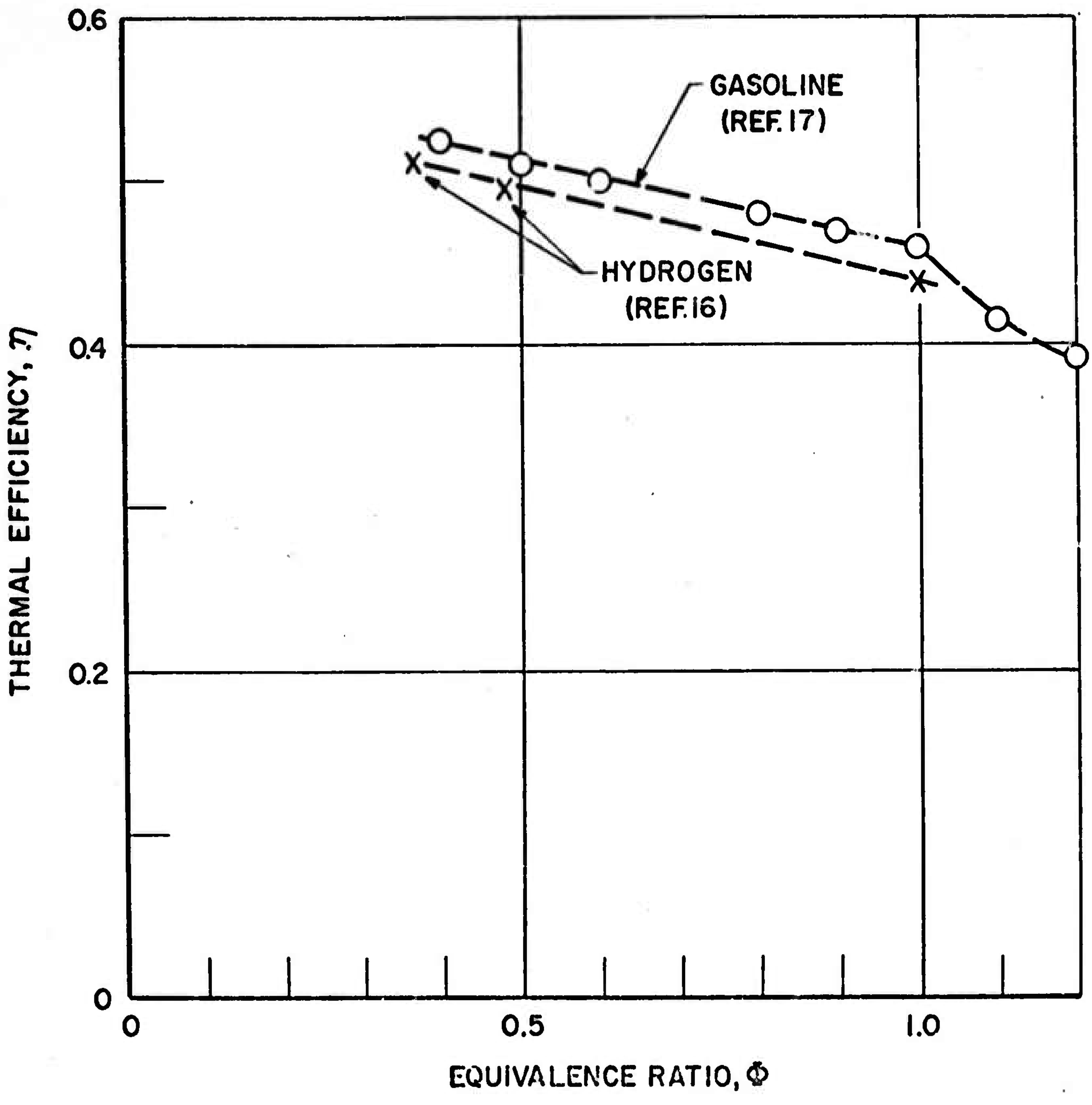

FIGURE C.3-3: Calculated Thermal Efficiencies of Non-CFI Gasoline/Air and H_2/Air Engines (Fuel/Air Cycle, CR = 10/1)

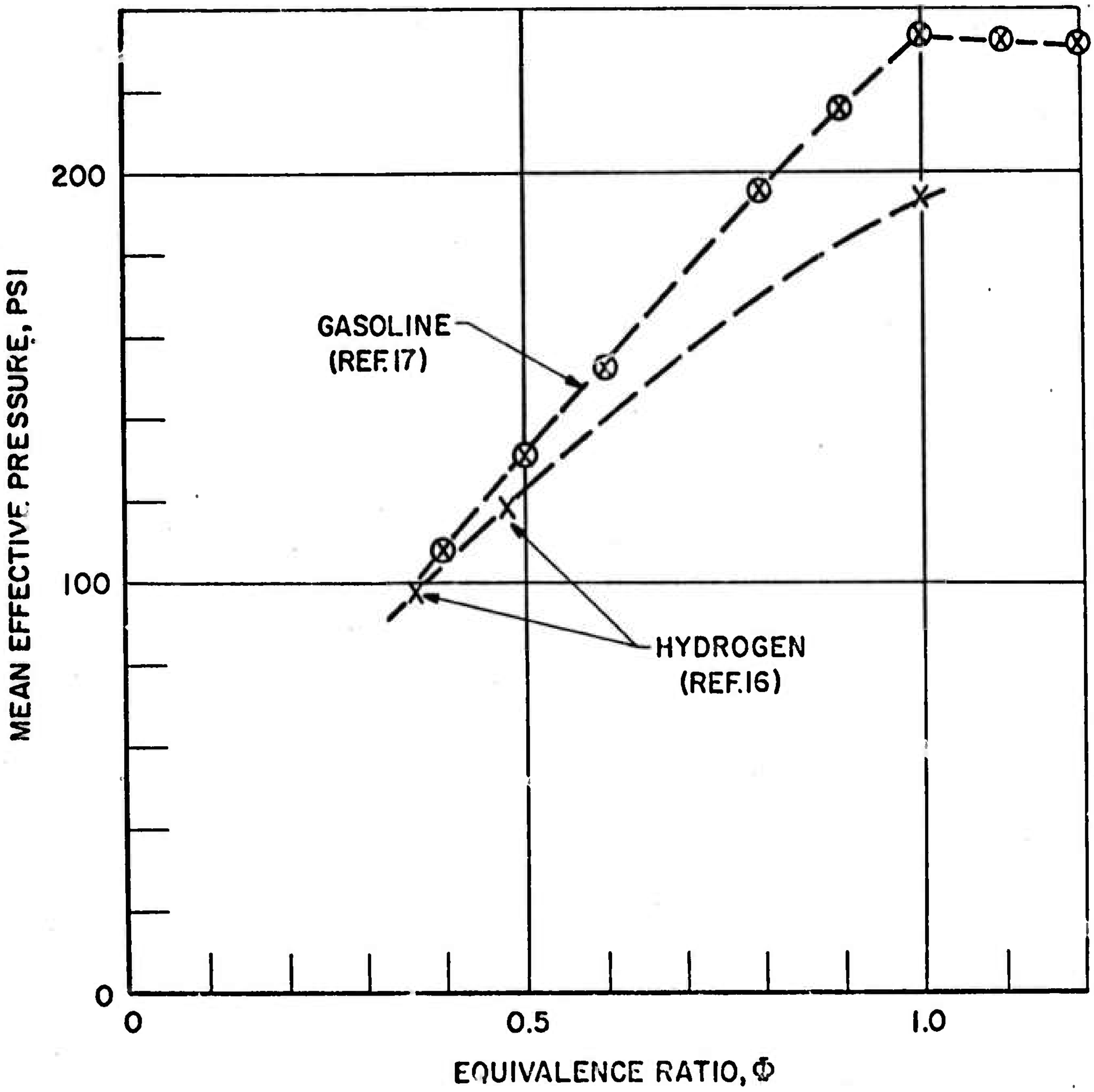

FIGURE C.3-4: Calculated Mean Effective Pressures of Non-CFI Gasoline/Air and H_2/Air Engines (Calculated from Fuel/Air-Cycle Efficiencies, CR = 10/1)

all the MEP values for hydrogen shown in the figure were calculated from efficiency values as explained earlier. To provide comparable gasoline-engine data, MEP's were calculated by the same method from efficiency data (even though directly calculated MEP data are available for gasoline; Ref. 17). The previously cited equivalence of volumetric efficiency in actual gasoline and hydrogen engines justifies this comparison of <u>indirectly</u> calculated MEP values. Fig. C.3-4 evidences the much discussed output-power penalty incurred by using hydrogen rather than gasoline; at $\Phi = 1.$, the MEP for hydrogen is approximately 20% below that of gasoline. At a given operating speed, a given engine displays power output proportional to MEP (by definition) and, therefore, at $\Phi = 1$ hydrogen-engine power could be expected to be about 20% below that from a gasoline engine. In consideration of Eq. 16, this 20% loss in power can be seen as deriving from a 5% decrease in efficiency and a 15% decrease in the chemical energy of the input charge to the hydrogen engine at $\Phi = 1$. As Φ decreases, the 15% chemical energy factor dwindles to nothing until, at low Φ, the chemical energy of the inlet charge is theoretically even higher with hydrogen than with gasoline. Fig.C.3-4 shows this.

While further comparisons of these incomplete MEP data can be made, it is not within the scope of the present report to do so. The significance of these values in a particular application requires considerations well beyond those relevant to the present summary and evaluation of operating experience. Such consideration will be more appropriate at a later point in the present program and will be given at that time.

<u>Exhaust emissions</u> from hydrogen-fueled engines have only recently been measured and reported as indicated by the total oxides-of- nitrogen ("NO_x") data of Table C.3-2. Table C.3-3 summarizes the reports of emissions other than NO_x.

Figure C.3-5 shows the NO_x data from "unmodified" engines (no EGR or WI) for which corresponding equivalence ratios are reported. In two cases (Ref's 9,10), NO_x emissions from a given test engine are reported for both gasoline and hydrogen operation. Also shown

TABLE C.3-3: Maximum Reported Emissions of CO and Unburned Hydrocarbons from Non-CFI, H_2/Air Engines (Attributable to Lube Oil Ingestion)

INVESTIGATOR	CO (gm/ihp-hr)	HC (gm/ihp-hr)	CONDITIONS
Finegold (Ref. 6)	0[1]	0[1]	1973 CVS test cycle
Breshears (Ref. 43)	<< .1	$\leq$ 1	ϕ = 0.2 to 0.46
Stebar (Ref. 10)	1.3	< .1	ϕ = 0.2 only; max. torque spark advance

Notes:
(1) Instrument resolution not specified

in Fig. C.3-5 are NO_x emissions calculated from peak NO_x concentrations (equilibrium) for hydrogen fuel-air cycles at a compression ratio of 9/1 (Ref. 18); the cycle efficiencies used in calculating gm/hp-hr from the NO_x concentrations of Ref.18 were taken from the calculated efficiencies of Ref 17 for CR=9/1. Calculated peak NO_x emissions from gasoline operation are very close to the values shown in the figure for hydrogen (Ref. 18).

The NO_x-emission data of Fig. C.3-5 (for unmodified engines) do not allow generalization excepting the trivial qualitative observation that emissions can probably be decreased substantially e.g., an order-of-magnitude, by operation at low equivalence ratio (e.g., $\Phi < .7$). This potential for NO_x reduction has often been cited based not only on the limited experimental data but also on the fact of decreased combustion temperature expected at low equivalence ratios.

At the equivalence ratios for which hydrogen and gasoline operation overlap, one set of data (Ref.9) show substantially higher emissions with hydrogen (by a factor of two or three or more) for one test engine. However, the data for gasoline operation of this test engine are substantially lower (by a factor of three to five) than reference test-engine data cited for gasoline (Ref. 19). A second set of comparative data (Ref. 10) is available, but only for $\Phi < 1.03$. These data show comparable emissions from hydrogen and gasoline engines until approach to its flammability limit causes the gasoline data to drop off, i.e., peak and decrease for $\Phi < 0.95$; the hydrogen data continue to rise with decreasing Φ, peaking at about $\Phi = 0.85$. Such comparisons cannot be considered conclusive at least without what is currently lacking, a well-based rationalization of the differences observed, the tendency, unfortunately, in reports of hydrogen-engine operation has been to focus on raw data without fundamental comparisons.

While still not allowing fundamental comparisons between gasoline and hydrogen operation, one investigation does allow further comparison in operationally significant terms. part-load power output. The data of Ref. 8 allow, at up to about 25% of rated load,

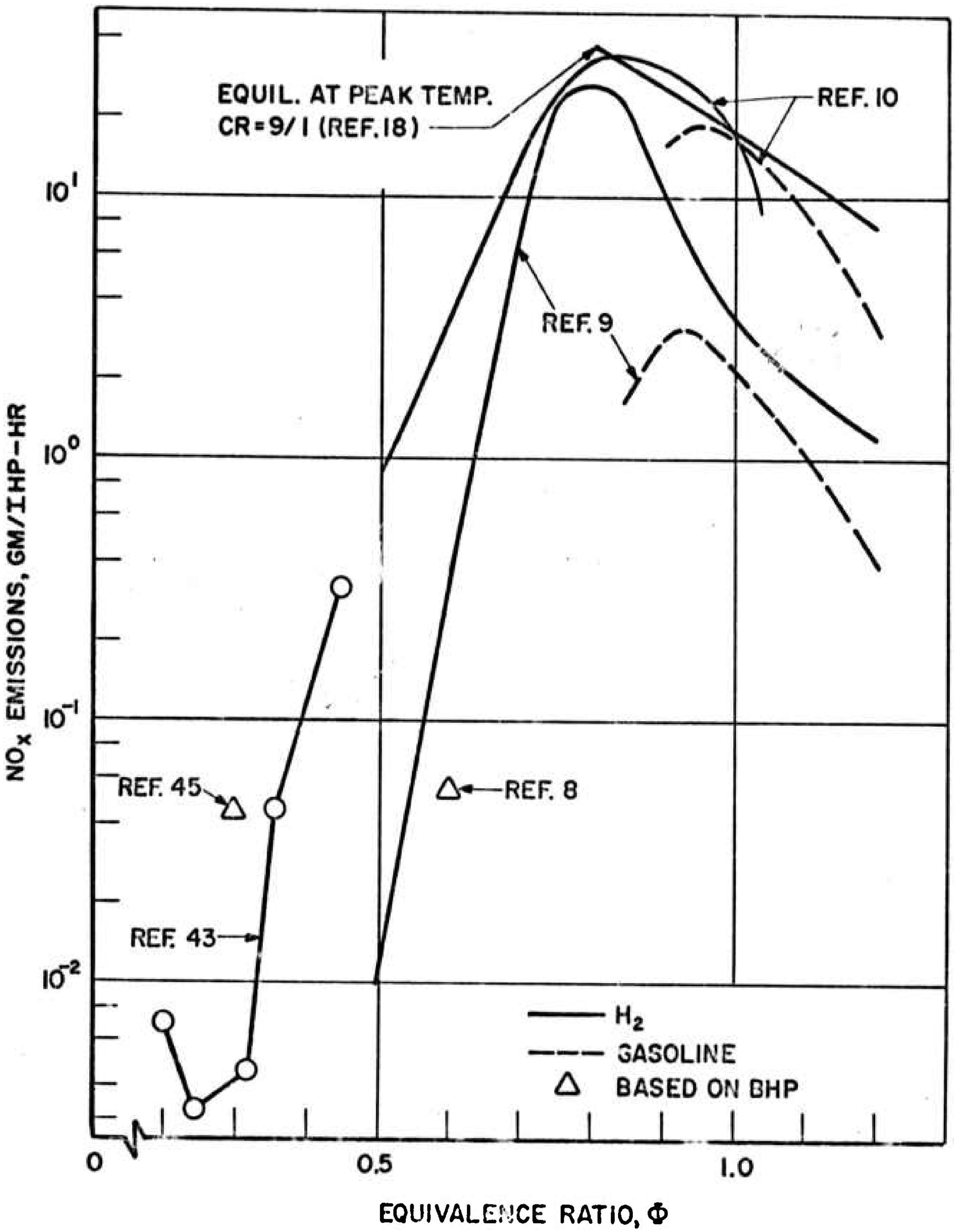

FIGURE C.3-5: NO_x Emissions From H_2/Air, Non-CFI Engine (With Comparison Gasoline-Engine Data)

a comparison of NO_x emissions with hydrogen and gasoline fuels both yielding the same power from the same engine.* NO_x emissions (ppm) with hydrogen are typically an order of magnitude below those of factory specifications (tuned operation) for gasoline at the same part-load output. Backfiring limited hydrogen operation to less than 25% of (gasoline) rated load.

Other performance factors reported from unmodified hydrogen-engine operation include:

(i) preignition and backfire (Ref's. 2,16,20-24)

(ii) autoignition (Ref's. 25,26)

(iii) combustion knock (Ref's. 2,16,22,27)

Preignition (ignition before spark-firing) and backfire (preignition before intake-valve closing) have been recurrent problems in hydrogen-engine operation, notably for equivalence ratios near 1. These phenomena are apparently a consequence of local hot spots or other "external" ignition stimuli. Early testing at low compression ratio (e.g., 5.45/1) gave preignition and backfire of fuel-rich hydrogen/air mixtures (Ref.20) and including slightly lean mixtures ($\Phi > 0.8$) (Ref. 21). Some tests at higher compression ratio (7/1) apparently allowed operation up to somewhat higher Φ (0.85) (Ref.21), but trends in preignition and backfire were not reported until the work of King (Ref's. 2, 16,22,23). Engine modifications (cool spark plug; aged, sodium-filled exhaust valve) were found to eliminate preignition and backfire at compression ratios up to 10/1 (Ref. 22) and finally to 14/1 (Ref.16) even for $\Phi > 7$. At compression ratios of 16/1 and above, however, preignition was found to persist at engine speeds above 1000 rpm (Ref.16) to the limit of testing, 1800 rpm, for $.80 < \Phi < 1.5$. Nonetheless, even at a compression ratio of 20/1, King was able to operate at a high enough equivalence ratio ($\Phi = .39$ to $.48$, depending on speed) to attain maximum efficiency,

* Brake thermal efficiencies are similarly compared.

though not, of course, high enough to give maximum power output ($\Phi = 1.0$). There are more recent reports of upper limits on equivalence ratios due to backfiring for operation of unmodified engines at both low compression ratio ($\Phi = 0.65$, CR = 5.5/1, Ref. 9) or higher ($\Phi = 0.6$, CR = 8.5/1, Ref. 8). Reportedly, backfire may occur (without preignition) even at much lower Φ (Ref. 22). Rationalizations of the influences of carbon from lube-oil pyrolysis, compression ratio, and combustion-chamber shape on preignition and backfire have been made (Ref's 15,16, 24,28). However, it cannot be said that the mechanism of preignition and backfire or even the qualitative influences of engine parameters on these is well-delineated.

Autoignition, in contrast with preignition, is a result of spontaneous ignition of the combustible-mixture, caused by the high pressures and temperatures achieved during compression of the mixture. For homogeneous combustible mixtures (carburetted), auto-ignition is important for two reasons. First autoignition could cause the mixture to "misfire" or ignite too early (during compression). This precludes spark-ignition control and causes peak pressures to occur too early, e.g., before the "top-dead-center" piston position, with consequent loss of power output. Second, autoignition of "end-gas" (before completion of spark-ignited burning) leads to "knock" and subsequent heat transfer and mechanical problems as well as power loss in engines.

Autoignition during mixture compression and before spark ignition has not been reported in hydrogen-engine work. Karim has reported autoignition measurements using a motored engine operated at 900 rpm with hydrogen, and lean limits of autoignition are reported (Ref. 25) for an inlet temperature of 300°F and for compression ratios above about 12/1 at $\Phi = .10$ to $.35$, depending on compression ratio. However, the timing of such autoignition is not reported, and it is not clear that this type of autoignition would interfere with "normal" engine operation. For example, King (Ref. 16) shows no evidence of pre-spark autoignition for CR = 14/1 and Φ as high as 1.25 or for CR = 20/1 with Φ as high as 0.5. King's lower intake temperature (65°F) and higher engine speeds

(1200 rpm or more) are, however, less favorable for autoignition than those of Karim. Autoignition misfires, without further investigation, cannot be discounted as a possible obstacle to high compression ratios.

<u>Autoignition knock</u> following spark ignition is a more common occurrence than the misfire autoignition just described, at least in hydrocarbon-fueled engines; commonly termed "detonation", it is a major, classic obstacle to gasoline-engine operation at high compression.

For hydrogen, the "highest useful compression ratio" ("HUCR") limited by the occurrence of knock, has been measured by several investigators (Ref's. 3-6, 29). Fig. C.3-6 summarizes the data. The HUCR approach is an alternative to the standardized octane-rating tests for gasolines. However, large variations are common if different operating conditions are used (Ref. 25), and standardized tests have not been specified and agreed upon.

Intake temperature variations change HUCR substantially for hydrogen, more so, for example, than for methane (Ref. 25); Karim's data for changes <u>only</u> in intake temperature show a variation of HUCR from 14/1 at 38°C (100°F) intake ($\bar{\Phi}$= 0.4) to HUCR of 8/1 at 150°C (300°F) intake (Φ =0.4). However, the data of Anzillotti <u>et al</u> for 40°C (104°F) and the data of Ricardo for 120°C (250°F) intake temperature show much better agreement and much higher HUCR's at a given equivalence ratio. Karim's lower values can be explained by the fact that his reported operations are for overadvanced, non-optimum spark advance (Ref. 25). Though the data are not highly consistent, it appears that elevated intake temperatures compromise HUCR more in hydrogen operations than in gasoline operation. Indeed, paraffinic gasolines show little "fuel sensitivity" (Ref.17), i.e., difference in octane rating between the "Motor" and "Research" knock-test methods, which differ substantially in intake temperatures (150°C <u>vs</u>. 50°C; 300°F <u>vs</u>. 125°F).

Knock arising from high rates-of-pressure-rise during normal combustion has been proposed by King (Ref. 16) as the source of knock in hydrogen engines (as distinct from the previously-cited

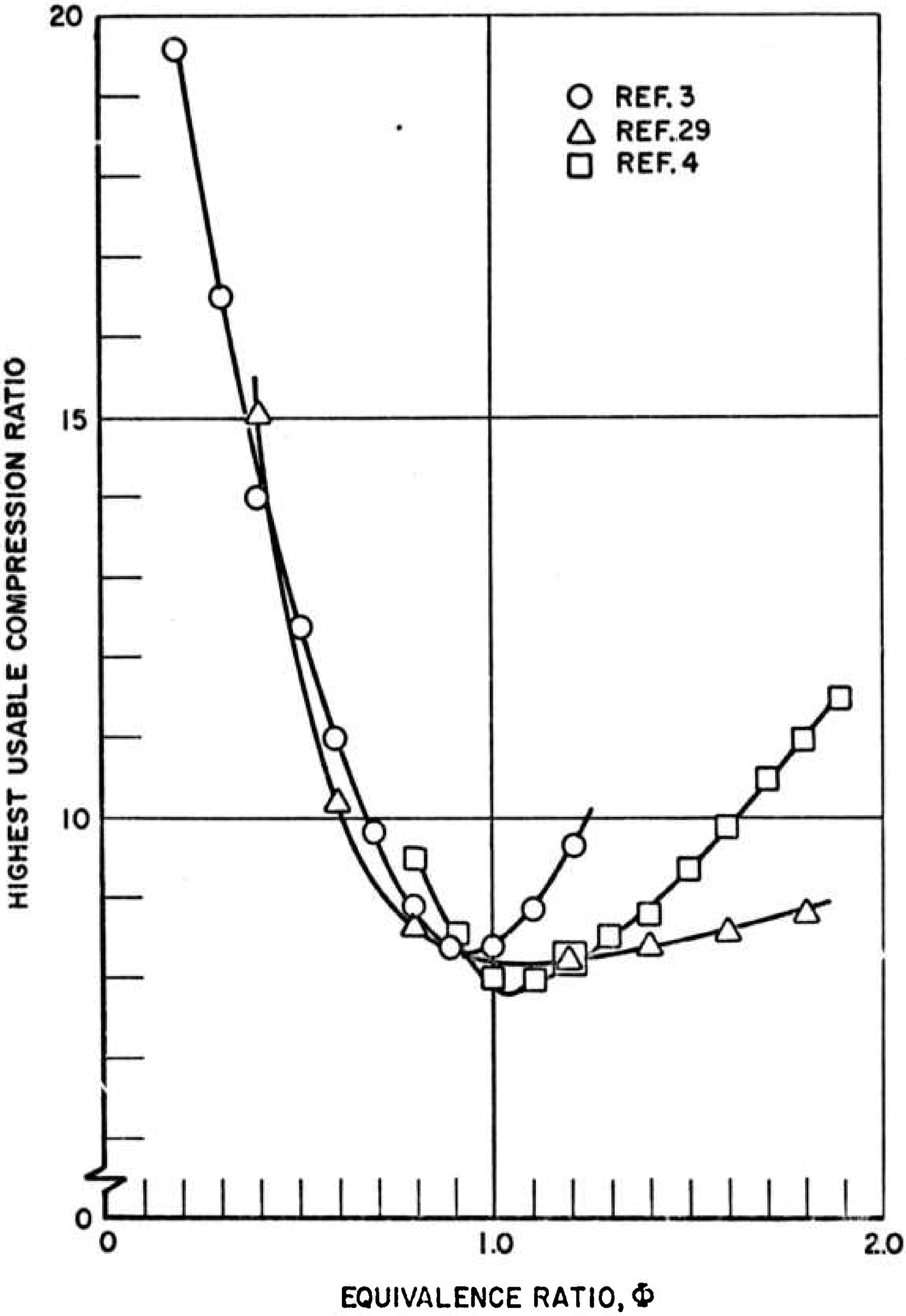

FIGURE C.3-6: Experimental Highest-Usable-Compression-Ratios for H_2/Air, Non-CFI Engines

autoignition knock involving premature ignition and burning of end gas). Pressure-time indicator diagrams for compression ratios as high as 14/1 show fast burning (of duration 1 to 2 msec, Ref. 16), and others have also reported short burning times. However, later experiments under knock conditions (Ref. 25) apparently showed classic autoignition knock at similar compression ratios, though at lower engine speeds (900 rpm) and somewhat higher intake temperatures (38°C; 100°F) than King's (1500 rpm, 65°F). King's proposal was based on limited experiments; his emphasis was apparently on distinguishing between normal combustion and true, gas-dynamic detonation. It is possible that his observations simply failed to uncover "normal" autoignition knock which was present. Indeed, his earlier reports of preignition knock ("detonation") due to hot spots (Ref. 2) displayed higher amplitude pressure oscillations than are common in usual autoignition knock. This may have led King to expect the same magnitude of oscillations during his later, knock-diagnosis experiments. Not observing oscillations of such magnitude during knock, he may erroneously have attributed knock to the high rates-of-pressure-rise of normal burning.

C.3.2.4-"Modified", Naturally-Aspirated, Spark-Ignition Engines

A small number of data largely at single operating conditions are available describing the performance of hydrogen engines modified with exhaust-gas recirculation ("EGR") (Ref's 6,8,9) or water injection ("WI") (Ref's 8,9). In gasoline engines and in hydrogen engines free of backfire, both of these modifications tend to decrease NO_x emissions (mostly due to decreased combustion temperatures). This occurs at the expense of decreased efficiency and power output (due to dilution). Small amounts of injected water may, however, increase efficiency and power output slightly (Ref. 9).

A major additional effect of EGR and WI in hydrogen engines is the elimination of backfire (Ref's 6,8,9). As a result of backfire suppression by substantial water injection ($M_{H_2O}/M_{H_2} = 2$), Finegold has reported from throttled hydrogen/air operation the

possibility of <u>increasing</u> power output in such a "quantity controlled" situation by decreased throttling before the occurrence of backfire (Ref. 8). This can be done reportedly without a major concurrent effect on efficiency, at least at $\Phi = 1$. In a "quality-controlled" operation, low levels of water injection, E.g., $M_{H_2O}/M_{H_2} = 0.3$) have been reported to eliminate backfire and simultaneously to increase power and efficiency slightly, at least for the given engine operating conditions (2900 rpm, $\Phi = 0.625$). In a "quality-controlled" hydrogen engine, these small gains presumably can add to observed increases in power (Ref. 9) provided by operation at a higher Φ with backfire.

In contrast, the elimination of backfire by EGR has not been shown to allow even slight intrinsic increases in power or efficiency at the same operating conditions. In at least one given operating condition, EGR elimination of backfire (25% EGR) has led to significant efficiency and power decrease (e.g., 5%). This is in accord with operating experiences with gasoline engines using EGR.

Unfortunately, the data presently available (both theoretical and experimental) are insufficient to clearly show any merits for EGR and WI in hydrogen engines aside from NO_x suppression. While NO_x suppression is apparent, the extent to which this is benefit trades off with efficiency and power output losses cannot presently be considered clear.

<u>C.3.2.5 - Supercharged Spark-Ignition Engines</u>

Supercharging is defined, for the purposes of this section to include not only the use of above-atmospheric manifold pressures but also "cylinder fuel injection"(CFI), the injection of gaseous hydrogen into the engine cylinder <u>after</u> closing of the intake valve. As does conventional manifold pressure supercharging, CFI hydrogen operation can allow engine operation with substantially greater air rates and therefore, higher MEP and power than otherwise is possible. As pointed out earlier (see Section C.2), the low density of hydrogen severely decreases the air rate of a carburetted or port-injected reciprocating engine compared with that

of a gasoline or even a hydrocarbon-gas engine. Direct injection into the cylinder allows the induction of pure air rather than a mixture during the intake stroke of a four-stroke engine. This allows the air rate of a low density hydrogen engine to be essentially that of a carburetted engine operated on a higher density fuel such as gasoline.

Supercharging via CFI operation is the subject of patents by Rudolf Erren in 1929, and Erren's pioneering work, summarized in Ref. 30 , is apparently the earliest reported use of hydrogen-engine supercharging of any kind.

Table C.3-4 designates those operating experiences which have involved hydrogen spark-ignition engines with CFI and for which at least a few data are available. There have apparently been no hydrogen-engine operations with conventional (manifold) supercharging, although plans for some have been made (Ref. 11). As the table indicates, scant operational data are available. This is due to the loss of Erren's records during World War II. The only substantial body of test data available today is that obtained by Murray and Schoeppel in 1971 on a modified, commercial, one-cylinder engine (Ref's 14,31).

Unfortunately, the major emphasis of the recent hydroen CFI-engine work is on demonstrating feasibility and pollutant emission levels of an injected engine. Significant data are missing apparently for this reason; only brake horsepower and efficiency data are presented. Lack of friction-loss and injection power-use data preclude direct calculation of indicated horsepower, MEP, and efficiency from the reported brake data. Particularly for the low-horsepower, modified engine which was used it is highly speculative to attempt generalization of the results by consideration of indicated, rather than brake power output and efficiency. For example, brake MEP's and efficiencies appear low for the circumstances, but might arise simply from unreported frictional losses and injection-power take off rather than from more fundamental effects of the fuel injection.

TABLE C.3-4a: SUMMARY OF CFI HYDROGEN/AIR ENGINE EXPERIENCE
ENGINE SPECIFICATIONS & POWER OUTPUT

INVESTIGATOR	NO. OF CYLINDERS	DISPLACEMENT (IN^3)	COMPRESSION RATIO	MAX. ENGINE SPEED (RPM)	MAX. PISTON SPEED (FT/MIN)	MAX. REPORTED POWER (HP)	MAX. POWER / DISPLACEMENT (HP/IN^3)	MAX. POWER / PISTON AREA (HP/IN^2)
Erren (Ref. 1)	-	-	8/1	-	-	-	-	-
Murray (Refs. 14,31)	1	8.3	6.5/1	4000	1250	2.8	.34 (1)	.63 (1)

NOTES:
(1) based on brake rather than indicated horsepower

TABLE C.3-4b: SUMMARY OF CFI HYDROGEN/AIR ENGINE EXPERIENCE - PARTIAL PERFORMANCE DATA

INVESTIGATOR	AT MAX. REPORTED POWER				AT MAX. REPORTED EFFIC.				PERFORMANCE CURVES?
	EQUIV. RATIO, Φ	THERMAL EFFIC., η (%)	MEP (PSI)	EXHAUST NO_x	EQUIV. RATIO, Φ	THERMAL EFFIC., η (%)	MEP (PSI)	EXHAUST NO_x (PPM)	
Erren (Ref. 1)	-	45	-	"none observed"	-	45	-	"none observed"	No
Murray Ref's 14,31)	1.89	12	76	340	.78	17	63	752	Yes

NOTES:
(1) based on brake rather than indicated horsepower

An even more fundamental shortcoming of Murray and Schoeppel's reported operating experience is that it remains to date unrelated to any fundamental theory dealing with the novel feature of their experience--direct cylinder injection. For example, it appears that a substantial fraction of the reported maximum power outputs may have come via the high-pressure gas-injection employed. This possibility is supported by a simple calculation of the power derivable from simple expansion of the high-pressure-injected hydorgen. Expanded through a volumetric expansion ratio (CR) of 6.5/1, the mass flow of hydrogen actually fed to the engine for a reported 2.3 hp output and MEP of 63 psi (at 3500 rpm) could yield about 0.5 hp or an MEP of about 13 psi simply by isentropic expansion. This kind of effect is also seen in Murray and Schoeppel's experimental data, i.e., in the reported monatomic increases in BMEP as equivalence ratio increases to about $\Phi = 2.3$. From a thermochemical, combustion viewpoint and from experience with non-injected hydrogen/air engines, one would expect a maximum MEP to be observed near $\Phi = 0.9 - 1.0$, owing mostly to the maximum in combustion temperature occurring at about $\Phi = 1$. Murray and Schoeppel's data do show a maximum exhaust temperatures for Φ near 1. In contrast, however, their data show the highest MEP's at higher Φ's, e.g., at the highest Φ tested, = 2.3. The monotonic trend of MEP with Φ indicates further that even higher MEP's could have been attained at $\Phi > 2.3$. In contrast with power output and MEP due to combustion, power output and MEP due to injected-gas expansion would be expected to increase monotonically, as was observed. This is because higher and higher Φ's require injecting more and more hydrogen at higher and higher pressures.

Still another problem in attempting to use Murray and Schoeppel's data to interpret the potential and problems of injected-hydrogen engines relates to NO_x emissions . Fig. C.3-7 shows Murray and Schoeppel's NO_x data for hydrogen and gasoline in the same engine. For comparison, NO_x concentrations from a gasoline test engine (Ref. 19) are shown as well as NO_x concentrations (equilibrium) calculated at peak cycle temperatures and pressures for both gasoline and hydrogen operation (Ref. 18).

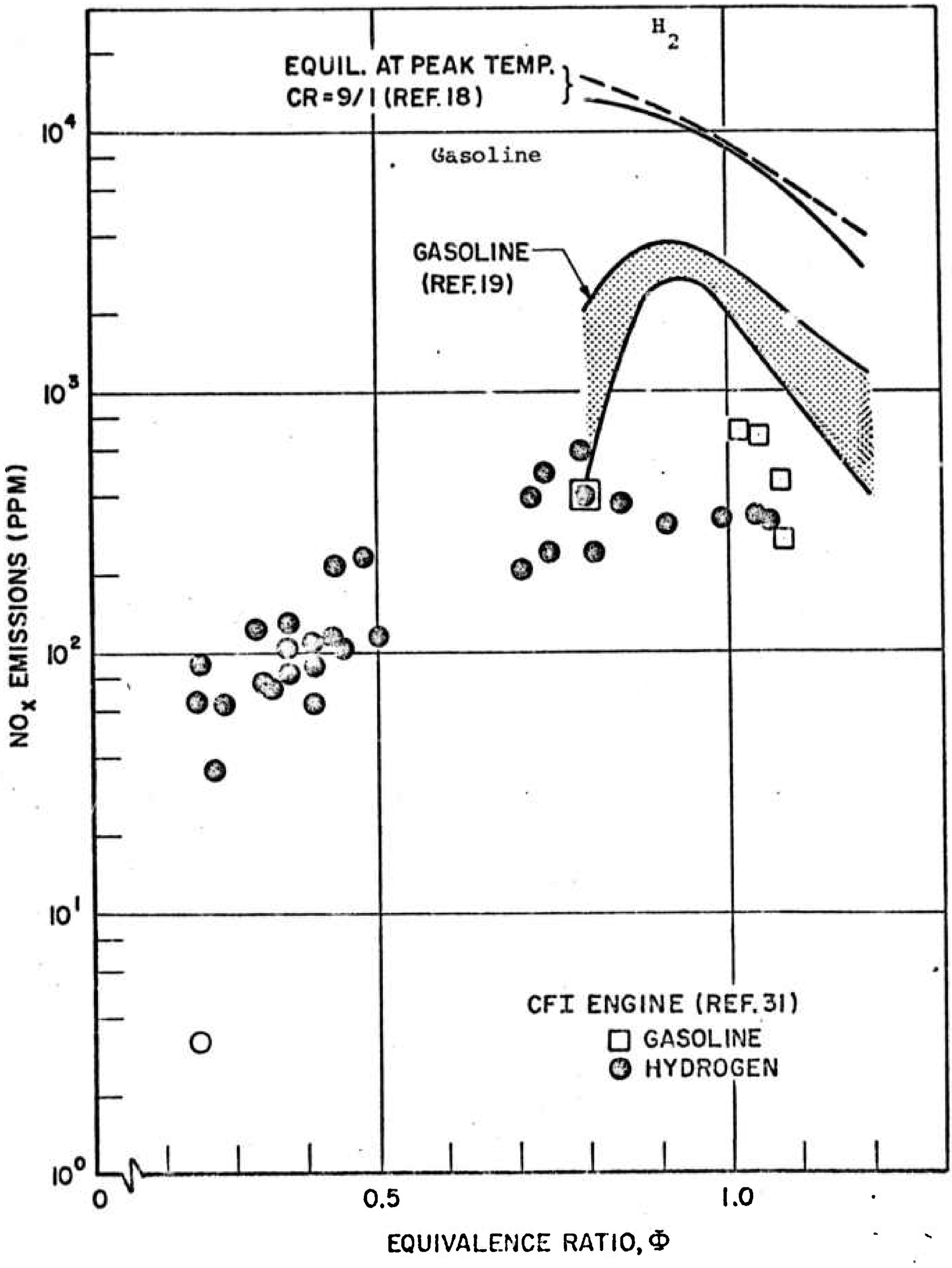

FIGURE C.3-7: NO_x Emissions from H_2/Air, CFI Engine (With Comparison Non-CFI Gasoline-Engine Data)

Comparison of Figure C.3-7 with Figure C.3-5 allows comparison of the data from Murray and Schoeppel's CFI engine with non-CFI H_2-engine data from other workers. In the "high" equivalence ratio range for which gasoline and hydrogen data are reported ($0.8 < \Phi < 1.1$), CFI reportedly yields NO_x emissions well below typical gasoline test engine data and carburetted-hydrogen-engine operation (see Fig. C.3-7). In contrast, at "low" equivalence ratios (where gasoline data are not available), Murray and Schoeppel's NO data are considerably higher than more recent data from other hydrogen engines (cp., Fig. C.3-5). Further in contrast, Murray and Schoeppel's data show a weak dependence of NO_x emissions on Φ at low Φ which is quite unexpected thermochemically and contrary to the trend exhibited by NO_x data from other hydrogen engines.

In summary, it appears that owing to the loss of Erren's records in World War II and the failure of Murray and Schoeppel to determine indicated power output and to interpret their data in fundamental terms, very little directly useful operating experience is available regarding injected-hydrogen (supercharged) air-breathing engines operated with CFI.

C.3.2.6 - Rotary-Combustion Spark-Ignition Engine

The only reported application of hydrogen as a fuel for rotary-combustion ("Wankel") engines is the demonstration project carried out at Brookhaven National Laboratory ("BNL") (Ref's. 32,33). For a demonstration and development of metal-hydride hydrogen storage, the BNL workers have operated a 8 hp. Wankel engine with hydrogen/air mixtures at several speeds (1000 to 4000 rpm) and loads. Performance data are sketchy owing to interest in the engine being peripheral to concern for metal-hydride storage (Ref. 34).

Brake thermal efficiencies and mean effective pressures for this Wankel engine operated on hydrogen are shown in Fig's. C.3-1 and C.3-2. The equivalence ratios shown were not measured but have been calculated using gasoline data for the same engine. Assuming an equivalence ratio for gasoline operation ($\Phi = 1.1$),

the air capacity of the engine can be calculated. Assuming no change in volumetric efficiency, Φ's for hydrogen were calculated from the reported hydrogen supply rates. Low mechanical efficiencies may be inferred from the calculated BMEP's and brake thermal efficiencies (compared with the other IMEP's and indicated thermal efficiencies of Fig's. C.3-1, C.3-2). These low values are probably not unreasonable for such a small engine, but lack of data concerning friction losses make it uncertain whether these hydrogen Wankel-engine data are actually consistent with other hydrogen reciprocating-engine data or not.

The BNL hydrogen-fueled Wankel engine operates smoothly and quietly from idle (approx. 900 rpm) to rates speed (4700 rpm).

C.3.2.7 - Compression Ignition Engines

The only data available concerning operating experience with pure-hydrogen-fueled compression ignition engines is apparently that of Helmore and Stokes (Ref. 35). While, to date this reference has not been obtained and reviewed, Gerrish and Foster (Ref. 36) describe some of Helmore and Stokes' results. While most discussion of these results is postponed to a later section on combined-fuel operation, some of the combined-fuel results are relevant to pure-hydrogen compression-ignition operation. Since these combined-fuel investigations apparently involved homogeneous rather than injected hydrogen/air mixtures, the following observations relate only to homogeneous-charge compression-ignition engines, not to common, injected, "Diesel" engines. There are apparently no data available from hydrogen-injection, compression-ignition engines.

Helmore and Stokes operated with combined fuel (90% hydrogen/10% fuel oil) only after violent detonation resulted during an attempt to burn pure hydrogen at CR=11.6/1. Unfortunately, Gerrish and Foster's citation is not clear on operating conditions for these tests. "Detonation at nine-tenths" full power appears to imply Φ =0.9 or perhaps slightly less.

Helmore and Stokes' "detonation" was presumably autoignition and, according to Karim's data on violently knocking autoignition, a maximum CR of about 13 is allowable without violent knock and

autoignition. Especially since such phenomena are dependent on configuration and test conditions, the differences between Karim's limit of 13 and Helmore and Stokes' 11.6 (at high Φ) are probably inconsequential. It appears that compression-ignition engines employing homogeneous mixtures are not practical owing to autoignition at least for Φ approaching 1. It must be noted at CR's exceeding approximately 12/1 that elevated intake temperatures may decrease this CR substantially, judging from Karim's data (Ref. 25).

Combined-fuel operations also have implications regarding pure-hydrogen operations. At compression ratios of 13.4/1 and 15.6/1 (Ref. 36), Gerrish and Foster found that hydrogen equivalence ratios could not exceed about 0.5 and 0.4,respectively, without preignition or backfire when small "pilot" changes fo fuel oil were injected (equivalent to $\Phi_{fuel\ oil}$=.022). This behavior may reflect the same phenomenon studied by King <u>et al</u> (Ref. 16) who found preignition and backfire attributable to solid carbon particles. However, at Φ of 0.5 and 0.4, homogeneous hydrogen/air mixtures would not compression-ignite without at least an "exceedingly small" pilot charge, for CR=13.4/1 and 15.6/1, respectively. The implication is that somewhere in the range $0.5<\Phi<0.9$, homogeneous compression-ignition operation is impractical for CR above about 14 or 15/1. This observation is consistent with King's observation in spark-ignition engines that backfire and preignition could be eliminated at CR=14/1 but occurred at CR≥16/1 for $\Phi \geq 0.8$.

Owing to lack of operating experience data, no generalizations can be made concerning injected-hydrogen compression-ignition engines.

C.3.3 - Hydrogen/Oxygen Engines

While a number of proposals for H_2/O_2 reciprocating engines have been made (e.g., Ref's. 37,38), operating experience is very limited and performance data sketchy. One of the most documented experiences is the development by Vickers, Inc. of an auxiliary power unit ("APU") for space application (Ref's. 39,40). An H_2/O_2 recip was considered promising for space application because of

its high specific power (small volume) and low specific weight. Otherwise, operations have apparently been limited to exploratory experiments and demonstrations rather than substantial performance testing (Ref. 41). Table C.3-5 summarizes the engine specifications and operating conditions for these H_2/O_2 engine operations. Also Table C.3-5 summarizes the performance data reported. Since there is virtually no data available from the experiments of the Perris Smogless Automobile Assoc. (Ref. 41), further consideration is limited to the operation of the APU.

The Vickers APU was operated with O_2 and H_2 injection and vacuum exhaust (for space application) and shows high specific power (4.75 bhp; 1.75 bhp/in^3, max.), brake thermal efficiency (0.32, max.) and bmep (173 psi, max.). Corrected by Vickers data for friction power, these data imply the maximum indicated power, specific power, efficiency, and MEP cited in the table. An additional correction is required to correct vacuum-exhaust operation to the more conventional ambient-exhaust conditions; with ambient exhaust, work is lost to compression of the exhaust residual by reactant injection. For the compression ratio used (12.7/1), however, this represents a negligibly small correction compared with that for the expansion work of the high-pressure-injected reactants (which is included in the brake thermal efficiency calculations by Vickers).

The APU engine was operated hydrogen-rich ($1.4 \leq \Phi \leq 7.0$) and was run over a range of speeds (2000 to 4000 rpm), indicated power outputs (0.75 to 5.28 hp), indicated MEP's (55 to 192 psi), and indicated thermal efficiencies (0.125 to 0.356) without exceeding design limits on cylinder-head temperature (apparently approx. 1400°F at an unspecified location). Heated hydrogen (500°F) was injected first at various supply pressures up to 400 psi followed by ambient-temperature oxygen at unspecified pressure (apparently 500 to 600 psi). Injection timing was not optimized. It appears that Φ was determined in each run as the minimum ($\Phi > 1$) consistent with maximum allowable head temperature.

TABLE C.3-5a: SUMMARY OF HYDROGEN/OXYGEN ENGINE EXPERIENCE - ENGINE SPECIFICATIONS & POWER OUTPUT

INVESTIGATOR	NO. OF CYLINDERS	DISPLACEMENT (IN^3)	COMPRESSION RATIO	MAX. ENGINE SPEED (RPM)	MAX. PISTON SPEED (FT/MIN)	MAX. REPORTED POWER (HP)	MAX. POWER / DISPLACEMENT (HP/IN^3)	MAX. POWER / PISTON AREA (HP/IN^2)
Morgan (Ref. 40)	1	2.72	12.7/1	4000	1025	5.15	1.9	3.0
Underwood (Ref. 41)	Various, few details given							

TABLE C.3-5b: SUMMARY OF HYDROGEN/OXYGEN ENGINE EXPERIENCE - PARTIAL PERFORMANCE DATA

INVESTIGATOR	AT MAX. REPORTED POWER			AT MAX. REPORTED EFFIC.			PERFORMANCE CURVES?
	EQUIV. RATIO, Φ	THERMAL EFFIC., η (%)	MEP (PSI)	EQUIV. RATIO, Φ	THERMAL EFFIC., η (%)	MEP (PSI)	
Morgan (Ref. 40)	6.	.32(1)	190(2)	Same as Max. Power			Yes
Underwood (Ref. 41)	-	-	-	-	-	-	No

NOTES: (1) Based on available O_2 in (rich) mixture and includes, as input, expansion work of H_2 supplied at 400 psig.
(2) Includes effect of expansion work by H_2 supplied at 400 psig, O_2 supplied at approx. 500 psig.

Since operations were with $\Phi > 1$, excess hydrogen acted as a diluent. Reported efficiencies were calculated as the ratio of power output to maximum available chemical energy (oxygen limited for $\Phi > 1$) plus the ideal expansion work available from the injected hydrogen. The potential expansion work of injected oxygen was not included though it appears to be comparable to that of injected hydrogen. Depending on operating conditions, varying fractions of available power (combustion plus expansion) were attributable to H_2 expansion: from about 5% ($\Phi = 1.4$) to about 15% ($\Phi = 6$).

It is reasonable to base the calculation of available combustion energy on the heavier reactant, oxygen, in space application where weight is a prime factor. In other applications, however, hydrogen cost or volume might be more significant, implying a need for efficiencies based on hydrogen supply rates and their associated potential for energy release through combustion. On the basis of hydrogen supplied, the reported efficiencies would apply only if excess hydrogen were recycled from the exhaust stream. Otherwise, efficiencies would be considerably lower than those reported:

$$\eta_{H_2 \text{ supplied}} = \eta_{O_2 \text{ supplied}} \frac{1}{\Phi}$$

i.e., for the reported maximum indicated efficiency (0.32) at $\Phi = 5.0$:

$$\eta_{H_2 \text{ supplied}} = (0.32) \frac{1}{5.0} = 0.053$$

Two alternatives exist to that of limiting operating temperatures in H_2/O_2 engines by using excess hydrogen ($\Phi > 1$). First, excess oxygen might be used ($\Phi < 1$). Second, another diluent might be used, e.g., recycled, condensed H_2O from the exhaust stream. While Karim has studied this possibility analytically (Ref. 38), there is apparently no operating experience bearing on these two alternatives.

C.3.4 - Mixed-Fuel Hydrogen Engines

Spark-ignition engines have been operated with mixtures of hydrogen and gasoline by several investigators (Refs. 10,20,42,43)

and with mixtures of hydrogen and kerosene (Ref. 20). Experiences with hydrogen and fuel oil in compression-ignition engines are also reported (Refs. 36,44). Mixtures of hydrogen with other gas fuels have also been tested (Refs. 15,35,47,50).

The most recent efforts have been with mixed-fuel spark-ignition engines and have been majorly concerned with extending hydrocarbon-fuel operation to lean mixture ratios (e.g. $\Phi = .5$) where pure gasoline and fuel oils will not burn easily. The impetus toward lean mixtures derives from the decreased NO_x emissions expected with low equivalence ratios (see section C.3.2.3 above). This gain is, of course, concurrent with an inherent loss of MEP (i.e., output torque and power) but with the likelihood of increased efficiency.

Ideally, one would compare performance data for the various mixed-fuel operations in a manner similar to that used above for hydrogen/air spark-ignition engines. Of course, an additional operating variable becomes influential, one expressing the mixed-fuel composition, e.g., the hydrogen mass-fraction of the mixture. Unfortunately, in two major reports of operating experience, values are not specified either for this variable (Ref. 43) or for some other significant variable (e.g., Φ, Ref. 20; MEP or power, Ref. 43). Even in one case where hydrogen fractions <u>are</u> reported (Ref. 10), the values are, at each value of Φ (for the mixture), the <u>minimum</u> hydrogen fractions observed to allow operation without misfire. While these lean-limit data on mixed-fuel operation are useful, they do not allow ready comparison with other data for different hydrogen fractions or from engines with different lean limits for misfiring. Some of the "missing" data required for meaningful comparisons can be back-calculated (by making reasonable assumptions). However, the results of such calculations have not, to date, allowed a satisfactory comparison to be made; unresolved discrepancies exist. In other cases, the "raw" data may be accessible though they have not yet been obtained. For these reasons, comprehensive treatment and comparisons for mixed-fuel operations cannot be reported at this time;

this section is concluded with a rough summary of operating experiences with spark-ignition engines emphasizing pollutant emissions.

Current efforts at the Jet Propulsion Laboratory (Ref. 43) and one report from General Motors Research Laboratories (Ref. 10) as well as a much earlier report by Ricardo (Ref. 20) corroborate the ability to operate hydrogen/gasoline/air spark-ignition engines at overall equivalence ratios as low as $\Phi = 0.1$. Below $\Phi = 0.6$, NO_x emissions are reduced to less than 0.4 gm/ihp-hr, fulfilling the Environmental Protection Agency 1977 standard. CO emissions are low enough (e.g., 4.5 gm/ihp-hr) at even higher Φ. Unburned hydrocarbons are, however, high, exceeding those of the EPA standard (0.5 gm/ihp-hr) for all Φ and exceeding the standard by a factor of 6 to 10 at $\Phi = 0.5$. Indicated MEP's appear to be about the same or somewhat above those for hydrogen operation particularly at Φ's near 1.0 where the mixtures used contain little hydrogen. Indicated thermal efficiencies, on the other hand, appear to be lower than with pure hydrogen operation by perhaps 3 to 5 percentage points. The collected data currently available are not unambigious, however, as regards both efficiency and MEP values, and further information and analysis are needed before a comprehensive view of mixed-fuel operations is available.

C.3.5 - References

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C.4 - SUMMARY

C.4.1 - Fundamental Considerations

Emphasizing air-breathing reciprocating engines, several basic performance relations are developed and it is shown that hydrogen engines, in comparison with conventional gasoline ones, are promising for high-efficiency operation, particularly when power is controlled by varying fuel/air ratio ("quality control"). Made practical by the relatively wide flammability limits of hydrogen/air mixtures, quality control with hydrogen allows high efficiency, low-emission operation at part load. However, the use of hydrogen leads to a penalty in maximum power unless steps are taken such as conventional supercharging or fuel injection into the engine cylinder following closing of the intake valve ("cylinder fuel injection", "CFI"). Without these, a power penalty arises from the low molecular weight of hydrogen which causes it to occupy a significant fraction (e.g., 30%) of the engine displacement volume, eliminating an equal volume of combustion air. With supercharging or CFI, it is feasible to achieve somewhat higher specific power from hydrogen-operation than from conventional gasoline-engine operation.

In addition to the theoretical elimination of CO and unburned hydrocarbon emissions, hydrogen operation shows promise for decreased NO_x emissions owing to the possibility of lean (quality-controlled) operation at part load. However, at full load (near stoichiometric mixture ratio), there is little rational basis for expecting substantially decreased NO_x emissions relative to comparable gasoline-fueled operation.

C.4.2 - Operating Experience

Operating experience is sufficient to show that non-CFI, H_2/air, reciprocating engine performance is generally consistent with the results of the limited thermodynamic analysis available at present. Presently available analysis is, however, insufficient to evaluate the limited operating data available regarding pollutant emissions or the performance of CFI, H_2/air; or mixed-fuel/air; or H_2/O_2 reciprocating engines. More analysis is needed and is planned as

part of the present program. Also notably lacking is sufficient experimental data to evaluate clearly several possible limitations on practical H_2-engine operation, for example, backfire, autoignition knock, crankcase contamination, long-term reliability, etc.

C.4.2.1 - H_2/Air Engines (Non-CFI)

Experimental data from naturally-aspirated H_2/air, reciprocating engines have been collected and scaled to a common compression ratio. The scaled values of indicated thermal efficiency (η) and mean effective pressure (MEP) as functions of mixture or equivalence ratio (Φ) have been compared with the results of fuel/air-cycle analysis for hydrogen and for gasoline. The highest reported values of η are higher in relation to theoretical fuel/air-cycled efficiencies for hydrogen (approx. 90%) than for gasoline (approx. 85%). However, theoretical fuel/air-cycle efficiencies for hydrogen/air are approximately 5% less than those for gasoline/air. The net effect is, then, that actual hydrogen and gasoline engines show approximately equal efficiencies at a given equivalence ratio of operation. Hydrogen can attain substantially higher actual efficiencies than gasoline only, because of hydrogen's potential for burning efficiently at leaner equivalence ratios. This is due to the lower lean limit of flammability for hydrogen/air ($\Phi = 0.1$) than for gasoline/air ($\Phi = 0.75$). Extension of the lean limit for gasoline operation by charge stratification, however, could decrease hydrogen's relative advantage in this regard.

While actual thermal efficiencies in hydrogen and gasoline engines are approximately the same, mean effective pressures are lower for hydrogen engines because of the lower chemical energy per cylinder charge with hydrogen. MEP's with hydrogen are about 20% lower at stoichiometric mixture ratios, but this difference decreases with decreasing mixture ratio, vanishing theoretically at $\Phi = 0.3$ to 0.4. Within the substantial uncertainty arising from experimental data scatter, volumetric efficiencies are apparently comparable with either hydrogen or gasoline operation. However, more comparable operating data are required with gasoline and hydrogen used in the same engine before definitive conclusions can be drawn.

As with thermal efficiency, NO_x emissions are probably comparable at a given equivalence ratio with either gasoline or hydrogen. However, data allowing direct comparison are scant. Hydrogen-engine emissions can be reduced by orders of magnitude by very lean operation (e.g., $\Phi \leq 0.5$), below the present lean-limit equivalence ratios for conventional gasoline engines (e.g., $\Phi \cong 0.75$). However, NO_x emissions can also be decreased substantially with gasoline engines by lean operation <u>via</u> charge stratification.

Compression ratios and equivalence ratios for practical hydrogen-engine operation with naturally-aspirated air can be limited by the phenomena of backfire, preignition, and/or autoignition. Compression ratios above 14/1 with $\Phi \cong 1.$ (for maximum power output) can be expected to be difficult to achieve without these phenomena occurring. Leaner operation does allow higher compression ratios and efficiency, though at the expense of substantially decreased mean effective pressure and power output.

A "rotary-combustion" (Wankel) engine has been easily adapted to hydrogen-fuel operation, but performance data are incomplete.

C.4.2.2 - H_2/Air Engines (CFI, Supercharged)

Very limited operating experience has demonstrated the feasibility of such an engine. The advantages of H_2 fuel can be gained without one of its major penalties, i.e., decreased MEP and power output (compared with carbureted hydrocarbon/air engines). The available performance data are, however, compromised in utility by the lack of a fundamental basis for interpreting them. Unexpected trends and values of both mean effective pressure and NO_x emissions need further clarification, both thoeretically and experimentally, before this engine's potential for low-emissions, quality-controlled, increased MEP operation can be considered well-established.

C.4.2.3 - H_2/O_2 Engines

H_2/O_2 piston engines have been operated fuel-rich in order to hold cycle temperatures down to practically low levels. Such operation (or, alternatively, fuel-lean operation) requires separation

of the combustion product, water, from the unburned reactant and recycling of the unburned reactant; otherwise, reactant wastage leads to very low efficiency. Even with such recycling, reported efficiencies (e.g., 32%) have not been notably high. Diluents (e.g., recycled water) can also be mixed with the reactants to obtain decreased cycle temperatures, but there is no apparent operating experience with such a system.

The major potential of H_2/O_2 engines is apparently in the possibility of high volumetric heat-release rates and of the elimination of product-gas pollutants. However, if diluents are used to limit cycle temperatures, these advantages, particularly the first, can be lost. Major drawbacks exposed to date include materials and design problems (e.g., sealing), largely related to the required hydrogen and oxygen reactant-supply and reactant-injection systems.

C.4.2.4 - Mixed-Fuel/Air Engines

Additive hydrogen has been demonstrated to extend the lean limits of flammability of gasoline, gas, and other fuels in spark-ignition engine operations. If substantial mass fractions of hydrogen are used (e.g., 0.2), operation at low equivalence ratio (e.g., 0.4) is possible. This makes quality control possible, at least as a supplement to quantity control, i.e., throttling. Gains in efficiency and substantial decreases in NO_x emissions are achievable compared to operation with pure hydrocarbon fuels. Compared to operation with pure hydrogen, mixed-fuel operation appears to show slightly lower efficiency at any given equivalence ratio while mean effective pressures are approximately the same or slightly higher with mixed fuels. The major engine-performance disadvantage in the use of additive hydrogen with hydrocarbon-fueled spark-ignition engines appears to be the unacceptable high levels of unburned hydrocarbons emissions for lean operation.

Efforts at viewing more comprehensively the performance of hydrogen-additive mixed-fuel operations with spark-ignition and other engines are impeded by incomplete experimental data. Work is currently progressing toward filling this gap by personal communication and/or approximate analysis.

C.4.2.5 - Compression-Ignition Engines

Aside from a small amount of data for mixed-fuel operations, almost no operating-experience data are available on hydrogen use in compression-ignition engines.

C.4.3 - Conclusions and Future Plans

The present summary of operating experience with various hydrogen engines is insufficient as a sole basis for evaluating the practicality and performance potential of hydrogen as a fuel for reciprocating engines. However, this collection of operating experiences (which is now virtually complete) serves as an imperative, first step in such evaluation. Several key areas demand, however, further attention. Consideration should be extended to include further analysis of the non-CFI engine (for which so much operating experience has been collected) and of the CFI engine (for which very little useful operating experience is available. Useful analysis should not only deal with the thermal aspects of hydrogen-engine performance (e.g., efficiency, MEP, etc.) but also with both mechanical-design parameters (e.g., piston and bearing loads, injector characteristics, etc.) and power-system parameters (e.g., fuel storage and supply systems, safety hazards, etc). Such efforts have been proposed for the next period of the present program.